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The Fate of Pharmaceuticals and Personal Care Products in Conventional and Engineered On-Site Wastewater Drain Fields

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THE FATE OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN CONVENTIONAL AND ENGINEERED ON-SITE WASTEWATER DRAIN FIELDS

by

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ABSTRACT

The Fate of Pharmaceuticals and Personal Care Products in Conventional and Engineered On-Site Wastewater Drain Fields

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Utah State University, 2013

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Improved analytical methods have led to the detection of pharmaceuticals and personal care products (PPCPs) in surface waters, and have resulted in an increased interest in the fate of these PPCPs. Interests include whether PPCPs can travel to drinking water sources and aquatic environments from wastewater treatment systems such as on-site wastewater treatment. Laboratory scaled columns were constructed to simulate a conventional pipe and gravel on-site wastewater drain field to investigate the fate of target PPCPs, including acetaminophen, caffeine, sulfamethoxazole, fluoxetine, carbamazepine, and progesterone. Over a span of 25 days, 200 liters of septic tank effluent spiked with 100 ng/mL of target PPCPs were pumped into the columns and sampled. Results showed that the PPCPs were non-detectable, except sulfamethoxazole, which peaked at a 74% concentration reduction, and carbamazepine, which stayed near the method detection limit (MDL).

Additional columns were engineered with similar design but a layer of charred straw or peat was placed at the bottom of the gravel layer to investigate PPCP removal enhancement. Similarly, septic tank effluent spiked with PPCPs was pumped into the columns and analyzed. Results showed that columns containing peat had a sulfamethoxazole concentration reduction plateauing at 81%, whereas concentrations decreased below the MDL in the columns containing charred straw. Similar to the columns without additional media, carbamazepine concentrations remained near the MDL and the other PPCPs were not detected. Overall, the experiment demonstrated that engineered on-site wastewater drainfields have the ability to reduce the concentrations of the target PPCPs.

Results from batch reactor experiments indicated that volatilization/hydrolysis is a minimal mechanism for target PPCP concentration reduction. Results also showed that sorption is the main mechanism for PPCP concentration reduction, with the exception of progesterone, where biodegradation is significant.

Isotherm experiments indicated that sulfamethoxazole sorption to soil is minimal and some isotherms could not accurately be produced including charred straw with acetaminophen, caffeine, fluoxetine, carbamazepine, or progesterone, and peat with progesterone, and soil with acetaminophen. Linearized Freundlich isotherms were generated for the remaining PPCPs with soil, peat, or charred straw being the sorbent. Overall, peat had the greater PPCP sorptive capacity.

(152 pages)

PUBLIC ABSTRACT

The Fate of Pharmaceuticals and Personal Care Products in Conventional and Engineered On-Site Wastewater Drain Fields

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Department: Civil and Environmental Engineering

Utah State University Division of Environmental Engineering student, under the direction of Ms. Judith L. Sims, has investigated the fate of six pharmaceuticals and personal care products (PPCPs) in conventional and engineered on-site wastewater drain fields. The presence of PPCPs in the environment, especially in aquatic environments, has raised awareness to the effects of PPCPs on aquatic life and the fate of these PPCPs, and has caused regulators to become more involved in setting requirements for the removal of PPCPs from wastewater.

This research investigated the fate of caffeine, acetaminophen, carbamazepine, sulfamethoxazole, progesterone, and fluoxetine in laboratory scaled columns that simulate conventional pipe and gravel on-site wastewater drain fields as well as engineered columns similar to the pipe and gravel simulated columns, but with the addition of media below the gravel layer to enhance PPCP removal via sorption and biodegradation. Results from the month long experiment showed that sulfamethoxazole removal in the columns representing conventional systems peaked at 74%. The other PPCPs were non-detectable. Sulfamethoxazole removal increased to 81% in columns engineered with a layer of sphagnum peat moss beneath the gravel layer and below the method detection limit (5.5 ng/mL) in columns engineered with a layer of charred straw

beneath the gravel layer. No other PPCPs analyzed from the engineered columns were detected. Batch experiments indicated that sorption is the main mechanism for PPCP removal with the exception of progesterone, where biodegradation is a major mechanism.

James Brent Beardall

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I figure more people are going to read this section than the actual study, so let me take the opportunity to give you the study in a nut shell: I put crap with drugs through a column of soil. The results were 1) that septic systems can do an okay job at decreasing those drugs, and 2) I earned a Master of Science degree. Now that that is out of the way, I acknowledge my major professor, Judith L. Sims, for her experience and lifetime's worth of expertise in on-site wastewater treatment. Judy is a wonderful professor who first took me and one of my greatest friends (Ashleigh) under her on-site wastewater tutelage over five years ago in order to help improve the lives of handicapped orphans in Mexico. This experience led to taking part in giving presentations at conferences, performing other studies involving on-site wastewater, and me earning an advanced degree. I am especially grateful for her trusting me with such a project and for her understanding when the process became frustrating. I acknowledge Dr. William Doucette for his patience in teaching me aquatic and organic chemistry…and then teaching it to me again four or five times till I finally got it. For also always keeping his door at least partially open at the lab and allowing me to ask him questions. I acknowledge Dr. R. Ryan Dupont for convincing me to go into environmental engineering and to keep at it when the courses increased in difficulty. For advising our Engineers Without Borders group that first sparked my interest in on-site wastewater and provided a wonderful opportunity to help those less fortunate than ourselves. I acknowledge Joe Stewart who helped me time and time again with the analysis even after I would constantly give him blank stares and Joan McLean who always made me feel

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CHAPTER I

INTRODUCTION

Over three millennia ago in the Knossos Palace in Crete, King Minos installed the first recorded flushing water closet (US EPA 2010). Toilets have also been found in Chinese tombs dating back to the Western Han Dynasty of 206 BC to 24 AD (Bellis 2011). On-site wastewater treatment systems evolved from pit privies to the more common conventional septic tank and soil absorption field. Septic tanks reduce traditional contaminants, such as biochemical oxygen demand (BOD_5) rich organic matter and total suspended solids (TSS), through settling and flotation and act as anaerobic bioreactors that promote partial digestion of retained organic matter (US EPA 2010). The liquid effluent from the septic tank is then discharged to gravel, soil, or other media absorption fields where the pathogen and nutrient rich effluent is further treated. On-site wastewater systems can function well as waste treatment units when properly designed, installed, and maintained for the incoming waste load and in areas with appropriate soils (US EPA 2010).

The 2009 American Housing Survey for the United States estimates that about ¼ of the population uses on-site wastewater treatment systems as a mean of sewage disposal (U.S. Census Bureau 2011). Regulations for the design of these on-site systems are mainly based on soil percolation tests, local practices and past experience, and are enforced by local public health departments (US EPA 2010). Some of these local practices, along with overtasked public health personnel, have resulted in some systems

being under-designed. The use of under-performing technologies has produced over a 1% failure rate. Failure, defined by the U.S. Census Bureau, means breakdowns where a system is completely unusable, such as a tank requiring pumping due to lack of effluent percolation (liquid removal via the drain field) i.e., clogged drainfield, tank collapse or explosion, or broken pipes (U.S. Census Bureau 2011). Not included in the survey were systems that might be contaminating surface or groundwater.

Improved analytical methods, leading to the discovery of pharmaceuticals and personal care products (PPCPs) in surface waters, have resulted in an increased interest in the fate of these PPCPs, specifically in whether PPCPs can end up in drinking water sources. In hospitals and households, pharmaceuticals such as antibiotics, antidepressants, analgesics, and hormones are used on a regular basis. After consumption or application, many drugs are non-metabolized and excreted into wastewater. Most wastewater is then treated by either a centralized treatment facility, such as a sewage treatment plant, or is treated on-site by an on-site wastewater treatment system or septic system. It is important to know whether PPCPs entering the wastewater stream will be removed or have the potential to enter the drinking water headworks.

Gravity flow systems are the most common and simplest method of wastewater distribution in on-site systems. A conventional drain field typically consists of an excavation filled partially with media, such as gravel, that stores wastewater (septic tank effluent), and allows it to percolate into the soil for further disposal and treatment (Figure 1).

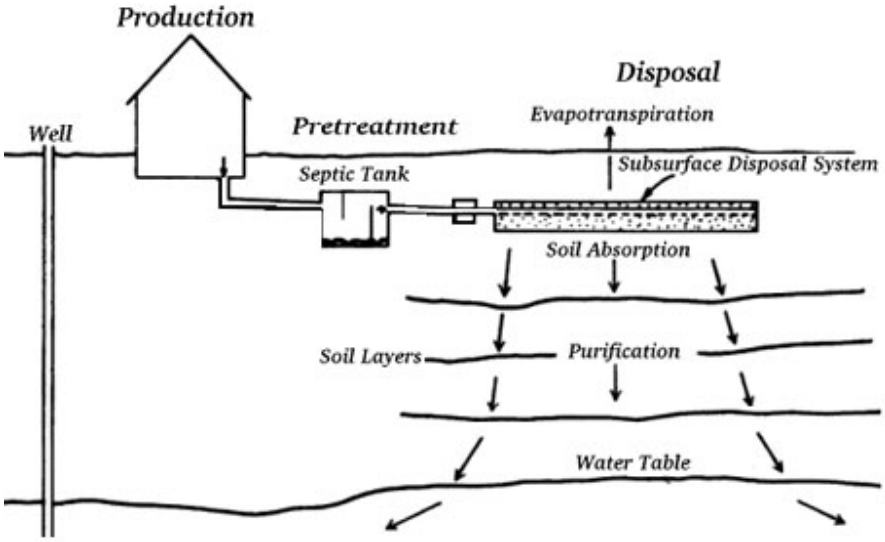


Figure 1: On-Site Wastewater Treatment (New Jersey Septic Management Group 2013)

The gravel supports the sidewall of the excavation, provides storage for peak wastewater flows, dissipates energy from incoming wastewater, and supports the distribution piping. The excavated area above the pipe and gravel is filled to the surface with natural earth or earth fill. Table 8 of the Utah Administrative Code R317-4 provides requirements for absorption trench construction (Appendix A) (The Department of Administrative Rules 2011).

This study investigated the fate of six selected PPCPs in a controlled laboratory setting by simulating a conventional gravity flow pipe and gravel on-site drain field and an engineered pipe and gravel drain field with the addition of sorptive media below the gravel. The engineered drain fields used in this study are similar in layout to the conventional drain field except that a two inch layer of media (sphagnum peat moss or charred straw) was placed below the gravel layer to provide additional sorptive sites.

The sorptive media used to further enhance PPCP removal that may already occur in the gravel drain field was sphagnum peat moss (Lakeland Canadian Sphagnum Peat Moss, purchased from Wal-Mart), a media often used in wastewater treatment; and charred straw, a less expensive alternative to granular activated carbon (GAC). Peat was used because it is known to have excellent ion-exchange properties and can host both aerobic and anaerobic bacteria, that enhance biodegradation (Allen et al. 2004). Surplus agricultural by-products such as soybean hull, sugarcane bagasse, and straw have been made into GAC and used for sorbing dissolved metals and organics (Johns et al. 1998). Wheat straw, an abundant local resource in Utah, was engineered by charring it to increase the surface area and increase the potential sorption sites. The charring was done by burning straw in a 50-gallon drum until the straw became ash.

The sandy/gravelly loam that was used in the study had a pH of 8.2 and organic matter that ranged from 0.5% to 0.7%. Other soil properties can be found in Appendix B. The peat had the greatest amount of negatively-charged sites available for sorption with a cation exchange capacity (CEC) of 30.1 cmol/kg, whereas the soil and charred straw had lower CECs of 7.2 cmol/kg and 6.5 cmol/kg, respectively. Septic tank effluent was collected from a septic tank with an average pH of 6.74.

Also included in the study are experiments investigating mechanisms that are most likely to contribute to PPCP removal, to better understand the fate of these PPCPs that can be used for future engineering of septic system drainfields.

The target compounds selected for this study were the stimulant caffeine, the analgesic/antipyretic acetaminophen, the anticonvulsant/antidepressant carbamazepine, the antibiotic sulfamethoxazole, the female hormone replacement progesterone, and

the antidepressant fluoxetine, commonly known as Prozac®, were chosen due to their high use, availability and presence in wastewater (AP Enterprise 2011).

CHAPTER II

LITERATURE REVIEW

Pharmaceutical products have triggered substantial concern because of their extensive occurrence in agricultural feedlots, groundwater, wastewater, and drinking water, their risk to human health, and their potential hazard to aquatic organisms. Pharmaceuticals are not only used to combat human and animal diseases but are widely used in farming and aquaculture.

Pharmaceuticals are designed to trigger specific biological effects and therefore pose a potential threat for aquatic species (Goebel et al. 2004). By nature, most PPCPs are biologically active and hydrophilic, so that the human body can more easily take them up. They are also often persistent in order to avoid degradation before they have a curative effect (Radjenovic et al. 2007).

Pharmaceuticals are excreted by users into wastewater. Depending on the compound and its properties, parent compounds and their metabolites are excreted via feces and urine. A literature review performed by Alcock et al. (1999) indicated that between 30 and 90% of an administered dose of most antibiotics is excreted via urine as active substance (Alcock et al. 1999). Calamari et al. (2003) indicated that up to 95%, such as was the case with the diuretic hydrochlorothiazide, of an administered dose of a pharmaceutical can be excreted as the parent compound.

Although concentrations released may be low (in the ng/L to µg/L range), their potential impact can be substantial, especially with substances that may accumulate in human tissue. Pharmaceuticals are designed to cause a response in humans and animals at low doses. However, steroids and estrogens, particularly those used in oral contraceptives, have high potency and can cause biological effects even at very low concentrations (Calamari et al. 2003). To estimate the potential amount of PPCPs being used, prescription data may be available via health insurance companies, but only rough estimations would be possible for those amounts of PPCPs used as medication in hospitals or sold as over-the-counter drugs (Heberer 2002).

PPCPs in the aquatic environment can cause reduction of breakage of eggs of birds, fishes, and turtles and can cause changes in the immunologic system of marine mammals, all which can lead to declines in populations (Esplugas et al. 2007). For example, fathead minnow were exposed to 4.0 ng/L of the PPCP 17 alpha-ethinylestradiol. After 56 posthatch days of exposure, the female to male sex ratio was 81:5. After 172 days posthatch, no testicular tissue was observed in any of the fathead minnows exposed (Laenge et al. 2001).

Although the concentration of individual drugs in the aquatic environment may be in the micropollutant range (sub-parts per billion), the presence of numerous drugs sharing a specific mode of action could lead to additive exposures that could cause significant effects. These effects may be of a more chronic nature because PPCPs are constantly introduced into the environment wherever humans are present (Daughton and Ternes 2000). Figure 2 shows possible pathways and sources for PPCPs in the environment.

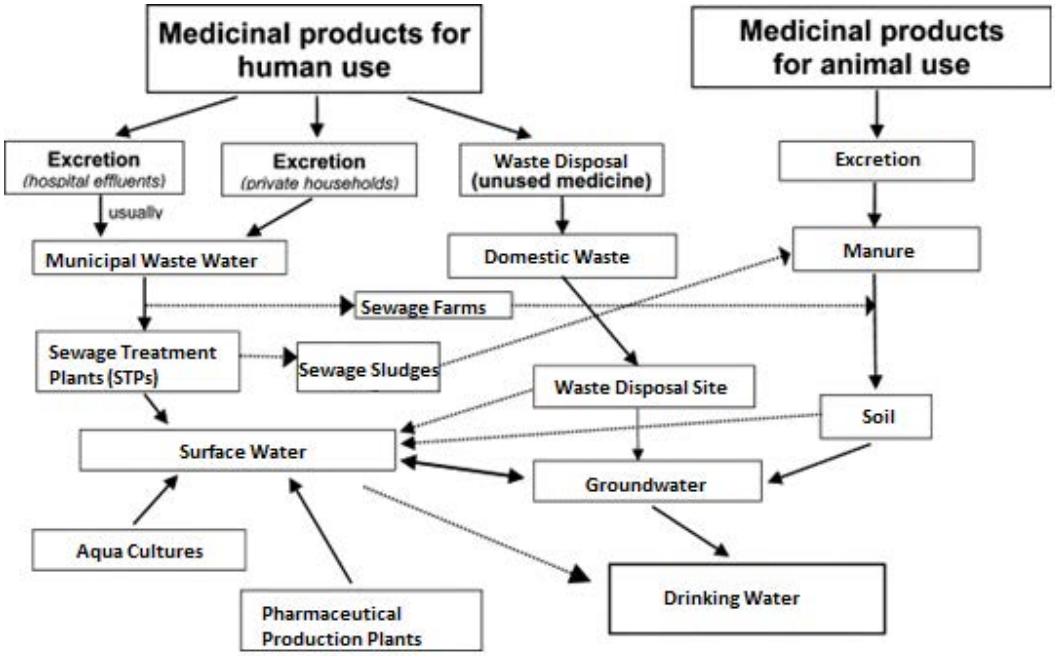


Figure 2: Possible PPCP Sources and Pathways (Heberer 2002)

Knowledge of the fate of PPCPS in groundwater, sewage treatment plants, drinking water treatment plants, and on-site systems can help understand the wastewater treatment methods that are most effective at PPCP removal, which in turn can help assess which groups, such as humans or aquatic species, are most at risk.

PPCPs in Groundwater

Under recharge conditions, that is, conditions where liquids percolate through soil to groundwater, PPCPs such as clofibric acid, carbamazepine, primidone, or iodinated contrast agents have been shown to leach through the subsoil and have also been detected in several groundwater samples (Heberer 2002). Drewes et al. (2007) performed a study investigating the fate of pharmaceuticals during groundwater recharge by measuring

groundwater samples from monitoring wells. The study revealed that caffeine was efficiently removed to concentrations below the detection limit (1-10 ng/L) in less than 6 months, whereas carbamazepine was not removed during groundwater recharge under either anoxic saturated, or aerobic unsaturated flow conditions during travel times of up to 8 years (Drewes et al. 2007).

Cordy et al. (2007) devised a proof-of-concept experiment to assess if PPCPs found in treated effluent could be transported through a 2.4 m soil column and thus potentially reach groundwater under recharge conditions. The total concentration of PPCPs introduced into the column decreased by more than 70%. Eight of the 131 compounds studied, including carbamazepine and sulfamethoxazole, were detected in all samples, indicating they have potential to reach groundwater under recharge conditions. Fluoxetine, acetaminophen, and progesterone were below their reporting limits (0.018, 0.009, 0.005µg/L respectively), and caffeine was reduced by 65% (Cordy et al. 2007).

PPCPs in Sewage Treatment Plants

Along with PPCPs excreted by users, unused PPCPs are sometimes disposed of into the wastewater stream via drains and toilets. Trace levels of PPCPs and their metabolites have been found in diverse sources such as sewage treatment plant effluents, surface waters, and even drinking water samples. Most PPCPs are not completely mineralized when they enter a sewage treatment plant. They are either metabolized to a still persistent hydrophilic form and end up in the receiving waters or they are retained in the sludge (Radjenovic et al. 2007). More than 80 PPCPs from diverse prescription classes have been detected up to the µg/L concentration in sewage (Heberer 2002). Ternes (1998) investigated the occurrence of 32 drug residues in municipal sewage

treatment plant (activated sludge with Fe(II)chloride coagulant) discharges. More than 80% of the selected drugs were detectable in at least one sewage treatment plant effluent with concentration levels up to 6.3 µg/L (carbamazepine), thus contaminating the receiving waters (Ternes 1998). The investigation concluded that given the relatively high stability of the medicinal compounds, the common sewage treatment process studied was not able to completely eliminate the drug residues. The PPCPs can then enter the aquatic environment and if not sorbed, biodegraded or otherwise eliminated, can potentially reach drinking water and also affect aquatic species.

Andersen et al. (2003) investigated the fate of estrogens in a sewage treatment plant with an activated sludge system for nitrification and denitrification with sludge recycling. They concluded that such a system can appreciably eliminate natural and synthetic estrogens, thus significantly reducing endocrine effect on aquatic species in the receiving waters. Elimination of natural estrogens exceeded 98% and largely degraded biologically in the denitrifying and aerated nitrifying tanks. Only 5% of the estrogens were sorbed onto digested sewage sludge (Andersen et al. 2003). Buser et al. (1999) performed a study looking at the occurrence of the pharmaceutical ibuprofen in surface waters and in wastewater. The three stage mechanical/biological treatment plants studied degraded the ibuprofen by 95% but concentrations up to 8 ng/L were still detected in receiving waters (Buser et al. 1999).

Goebel et al. (2004) developed an analytical method for the simultaneous trace determination of four macrolide antibiotics, six sulfonamides, and some of their metabolites in wastewater. They concluded that because none of the analytes were fully eliminated during conventional activated sludge treatment followed by sand filtration,

that trace amounts of these PPCPs reached ambient waters. In the case of sulfamethoxazole, only 70% of the compound was eliminated (Goebel et al. 2004).The occurrence and sorption behavior of sulfonamides and macrolides in activated sludge treatment was later investigated by Goebel et al. (2005) and it was assessed that sorption of the investigated antimicrobials to activated sludge was low (below 500 L/kg) (Goebel et al. 2005).

The solids retention time at a sewage treatment plant is an important parameter that can relate growth rate of microorganisms to effluent concentrations. Sewage treatment plants operating at higher solids retention time (a minimum of 10 days) can encourage the degradation of PPCPs (Clara et al. 2005), whereas some PPCPs, such as carbamazepine, can still pass the bioreactor without any changes (Clara et al. 2003). Moehle and Metzger (2000) performed a screening and biodegradation study of drugs in municipal sewage effluent. They attributed the "fast elimination" (within 15-30 minutes) of several compounds primarily to sorption on the activated sludge. The study showed that a slow decrease of concentration of compounds, such as caffeine, could be observed within several hours or days until concentrations were less than 1% of the initial concentration, which was attributed primarily to primary degradation (Moehle and Metzger 2000).

PPCPs are not completely eliminated from sewage treatment plants; therefore they have the potential to reach receiving waters for drinking water sources.

PPCPs in Drinking-Water-Treatment Plants

Because groundwater influenced by septic system effluent could end up in headwaters to drinking-water-treatment plants, it is important to know the potential

treatment of PPCPs by drinking-water-treatment plants. Stackelberg et al. (2004), as part of a US Geological survey project, conducted a study to evaluate the persistence of PPCPs in a conventional drinking-water-treatment plant. Samples were collected at locations within the treatment plant and from the two streams that serve the facility and are partially sourced by an upstream municipal sewage-treatment plant. Each sample was analyzed for 106 PPCPs including sulfamethoxazole, acetaminophen, caffeine, fluoxetine, and carbamazepine. Forty PPCPs were detected in stream water samples or raw-water supplies in the treatment plant, 34 were detected in more than 10% of the samples from within the plant, and as many as 17 PPCPs (including caffeine and carbamazepine) were detected in samples of treated water (Stackelberg et al. 2004).

PPCPs in On-Site Wastewater Treatment Systems

Singh et al. (2009) performed a comprehensive survey of human waste contamination markers in the South Florida and Florida Keys areas heavily reliant upon the use of septic systems. The study documented the occurrence and distribution of selected hormones, steroids and commonly detected pharmaceuticals in surface water samples. One of the most common compounds detected was caffeine at concentrations ranging from 5.5-68 ng/L (Singh et al. 2009).

In Ireland on-site systems are a common way to dispose of wastewater effluent. A study performed by Ó Súlleabháin et al. (2008) analyzed wastewater effluent from an on-site drain field using lysimeters and found low concentrations of endocrine disrupting compounds, such as octylphenol (~50 ng/L) and estrogens (~2.0 µg/L) at four different sampling sites (Ó Súlleabháin et al. 2008).

Conn et al. (2006) performed a study looking at the occurrence of organic contaminants, such as surfactant metabolites, steroids, stimulants, metal-chelating agents, disinfectants, antimicrobial agents, and pharmaceuticals, during on-site wastewater treatment. Thirty on-site wastewater treatment systems (22 tank-based treatment systems, seven biofilter-based treatment systems, and one subsurface-flow constructed wetland), consisting of both subsurface soil infiltration trenches and above-ground mounded soil systems, representing a range of both residential (single- and multi-family homes) and non-residential (food establishments, elementary schools, and veterinary hospitals) sources, were sampled for the organic contaminants. The samples were collected once in the fall and once in the spring, mostly from mid-depth at the outlet of each tank, whereas some samples were collected from the tank inlet, textile filter units, and the subsurface constructed wetland. Eighty-eight percent of the 24 target compounds were found in one or more of the on-site wastewater samples and several compounds, including caffeine, were detected in every wastewater sampled. The study found caffeine (<0.5-320 µg/L) in 98% of samples analyzed. One of the multifamily residential tank-based systems was analyzed for additional organics and found elevated levels of acetaminophen (45 µg/L) and low levels of carbamazepine (0.0048 µg/L) in the septic tank effluent (Conn et al. 2006).

Carrara et al. (2008) examined three high volume septic systems (one serving 500,000 day visitors per year, one serving 200 campsites, and the other servicing 2000 guests annually) to assess the potential release of pharmaceutical compounds to the environment. Concentrations of Ibuprofen, salicylic acid, gemfibrozil, nanproxen, triclosan, ketoprofen, diclofenac, indomethacin, and bezafibrate found in the septic tank

samples were also detected in groundwater at one or more sites at concentrations ranging from the low ng/L to µg/L. Compounds at greatest distances from the infiltration source areas and at highest concentrations were observed to be particularly in anoxic zones (Carrara et al. 2008).

Godfrey et al. (2007) assessed the occurrence and persistence of 22 target pharmaceuticals in septic tank effluent and two shallow, coarse-grained aquifers in western Montana. Twelve compounds, including acetaminophen, caffeine, carbamazepine, and sulfamethoxazole were detected in a high school septic tank effluent with concentrations of carbamazepine and sulfamethoxazole up to 450 ng/L and 29,000 ng/L respectively. Carbamazepine and sulfamethoxazole were detected at concentrations up to 210 ng/L and 450 ng/L respectively in the underlying sand and aquifer after having percolated through a 2.0 meter thick sand vadose zone (Godfrey et al. 2007).

Swartz et al. (2006) monitored several organic wastewater contaminants to groundwater in a residential septic system and in down gradient groundwater. Two of the contaminants included caffeine and its degradation product paraxanthine. Caffeine and paraxanthine were up to a 60-fold lower concentration in the near-source suboxic to anoxic portion of the wastewater plume versus the septic tank, suggesting a net removal of these constituents in the drainfield (Swartz et al. 2006).

Similar to studies conducted on on-site systems, a study was conducted using soil that received treated effluent from a sewage treatment plant. The soil was analyzed for PPCPs, including caffeine and estrogens. PPCP concentrations in the soil ranged from non-detect to 319 ng/g (Karnjanapiboonwong et al. 2011). Sorption and degradation of six PPCPs was investigated using agricultural soils associated with reclaimed wastewater

reuse. Experiments demonstrated that sorption could be described with the Freundlich equation. Degradation of the six PPCPs in soil generally followed first-order exponential decay kinetics, with half-lives ranging from 0.81 to 20.44 days. Soil organic matter, clay content, and microbial activity played a significant role in the degradation of the PPCPs in soil (Xu et al. 2009).

Similar to sewage treatment plants, on-site wastewater treatment systems do not completely remove PPCPs from the waste stream. Soil used in on-site wastewater treatment systems, however, showed an increased ability to sorb and degrade PPCPs, depending on the soil's properties such as organic matter and clay content.

Treatment Media

Many wastewater, drinking water, and on-site wastewater treatment systems have used either organic materials, such as peat or activated carbon, to treat their respective water sources. The organic materials can catalyze biodegradation as well as have sorptive properties, whereas the activated carbon primarily enhances sorption.

Although traditional activated carbon was not used in this experiment, the charred straw that was used was chosen as a similar, less expensive alternative that may have PPCP reducing properties similar to that of traditional activated carbon. Charred straw and traditional activated carbon are similar in that they are both generated by burning carbon rich products such as bone or straw. The major difference is that traditional activated carbon is generated without oxygen whereas straw for this experiment was charred in a barrel open to the atmosphere. It was not expected that charred straw would be as efficient at removing PPCPs as traditional activated carbon but was expected to have some PPCP removing characteristics.

Peat in Wastewater Filtration

Peat is a polar, highly porous (approx. 95% porosity, with a specific area of 200 m^2/g) material that can be inexpensive and easy to use for wastewater filtration. Peat comes from partially fossilized plant matter that is formed in poorly oxygenated wetlands, where the rate of plant matter accumulation is greater than that of decomposition (Couillard 1994). Peat is a complex material with cellulose and lignin as prime constituents. Peat's polarity comes from functional groups in the lignin such as alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers that are involved in the formation of chemical bonds (Couillard 1994).

Peat has been used as a low-cost method for removing dyes from effluents with varying pH (Nawar and Doma 1989). Toller and Flaim (1988) performed a study examining the use of peat in a filtering unit for the removal of pesticide residues from aqueous solutions. The filter was used to treat pesticide mixtures generated during agricultural operations before being discharged into open waters. The filter was capable of filtering out more than 99% of almost all of the pesticides applied. The exception was the highly water soluble (4kg/L) pesticide vamidothion, which had a percent removal between 40 and 70% (Toller and Flaim 1988).

Peat was first used for filtering wastewater in Virginia, Minnesota in the 1970s at a USDA Forest Service campground in the Chippewa National Forest and has been used successfully for over 20 years (Geerts and McCarthy 1999). A characteristic peat filter system uses a pre-fabricated container or a lined excavation with an under-drain system composed of a few inches of gravel, then a larger layer (24-36 inches) of peat. Distribution piping delivers wastewater to the peat filter where it is filtered before being discharged to a drainfield. Peat provides an excellent environment for many different

kinds of both aerobic and anaerobic bacteria. Peat filters can be operated similar to sand filters in that they can be single pass or a re-circulating filter. They can also perform well at removing organic matter (>90% removal), solids (>90% removal), pathogens (>99.99% fecal coliform removal), and, depending on recirculation, nutrients (23-61% phosphorus removal, 22-67% total nitrogen removal) (Geerts and McCarthy 1999).

Straw in Wastewater Treatment

Straw that has been chemically modified with a cationic surfactant has been used to remove emulsified oil from wastewater (Ibrahim et al. 2010). Waste sugarcane bagasse has been charred for sorption enhancement and has been used to separate heavy metals such as cadmium, lead, nickel, zinc, and copper from aqueous solutions (Homagai et al. 2011).

CHAPTER III

CHEMICAL INFORMATION

In order to understand or estimate the potential movement and alteration of a chemical, an understanding of the chemical's properties is required. Useful chemical properties from the PPCPs used in this study are described in Table 1. One way to assess the potential fate and transport of chemicals is by using models. The Estimation Program Interface Suite™ (EPI Suite) is a Windows®-based suite developed by the Environmental Protection Agency's Office of Pollution Prevention and Toxics, and the Syracuse Research Corporation (US EPA 2011). EPI Suite has a database of physical/chemical properties and an environmental fate estimations program. The environmental fate estimation program contains a level III multimedia fugacity model that predicts partitioning of chemicals among air, soil, and water under steady state, but not equilibrium, conditions. Half-life, advection, and Soil K_{oc} values were estimated by EPI Suite, whereas emission values were modified to 0.008kg/hr to the soil to fit the studies application.

EPI Suite also contains a program that predicts the removal of a chemical in a typical activated sludge-based sewage treatment plant (Sewage Treatment Plant Model). The values given for total removal are assumed to be contributed by biodegradation, sorption to sludge, and air stripping. Although an activated sludge-based sewage treatment system is a different technology from an on-site wastewater system, they both have the potential for biodegradation and sorption as dominant means of wastewater treatment, especially in the case of relatively soluble PPCPs.

Other models that make up EPI Suite contain estimates for partition coefficients, biodegradability, and chemical constants.

Table 1: PPCP Properties

PPCP	Elemental Composition	K_{OW}	Solubility (mg/L)	pKa	Speciation Charge in Study System	Henry's Constant (atm-m^3/mole)
Caffeine	C-49.49%; H-5.19%; N-28.85%; O-16.48%	0.85	21,600	0.5	Neutral	3.58E-11
Acetaminophen	C-63.56%; H-6.00%; N-9.27%; O-21.17%	2.88	14,000	9.48	Mostly Neutral, very little negative	6.42E-13
Carbamazepine	C-76.25%; H-5.12%; N-11.86%; O-6.77%	281.8	112	2.3	Neutral	1.08E-10
Sulfamethoxazole	C-47.4%; H-4.4%; N-16.6%; O-18.9%; S-12.7%	7.76	610	1.7, 5.7	Mostly negative, some neutral	9.56E-13
Progesterone	C-80.2%; H-9.6%; O-10.2%	7,413	8.81	NA	Neutral	6.49E-08
Fluoxetine	C-59.09%; H-5.54%; F-16.48%; N-4.05%; O-4.63%; Cl-10.25%	11,220	61	9.53	Mostly positive, very little neutral	8.90E-08

Another tool used for gaining an understanding of a chemical's state is the University of Georgia's Sparc Performs Automated Reasoning in Chemistry (SPARC)

program (Hilal et al. 2011). SPARC can be used to estimate acid dissociation constants and plot chemical speciations. This information, along with a septic tank pH of 6.74 and a drainfield pH of 8.2, is then used to evaluate which species (charged, uncharged, or neutral) will be dominant and help predict the chemical's ability to sorb to media.

Although no one model will be able to completely simulate the conditions of an on-site wastewater drainfield, a combination of estimates from the various models can help organize information about the PPCPs used in this study, which could be used to hypothesize their fate. The following sections describe the selected PPCPs used in this study.

Caffeine

Caffeine has a white powder appearance or white, "glistening needles," usually matted together. It has a bitter taste and is odorless. Caffeine is a weak base that is neutral in most environmental systems (Zubair et al. 1986).

Caffeine is a purine alkaloid stimulant found in various drinks, chocolate, nuts, and medicines. The stimulant can make a person more alert and provide a boost of energy. Drinks such as a generic 8 oz. coffee can contain an average anywhere from 95 to 200 mg/L of caffeine whereas sports drinks may have upwards of 280 mg/L of caffeine. The pain medication Excedrin® (extra strength) contains around 130 mg/L of caffeine and the alertness pill NoDoz® contains 200 mg/L of caffeine (Mayo Clinic 2009). Caffeine has metabolic effects such as stimulation of the central nervous system, the release of free fatty acids from tissue and increased urination (American Heart Association 2010). For humans, the plasma half-life is between 4 to 10 hours and 45% of

a dose is usually excreted in urine within 48 hours as 1-methylxanthine and 1-methyluric acid. Other breakdown products excreted in the urine can include theophylline, 1,7-dimethylxanthine, 7-methylxanthine, 1,3-dimethyluric acid and some unchanged caffeine (Zubair et al. 1986).

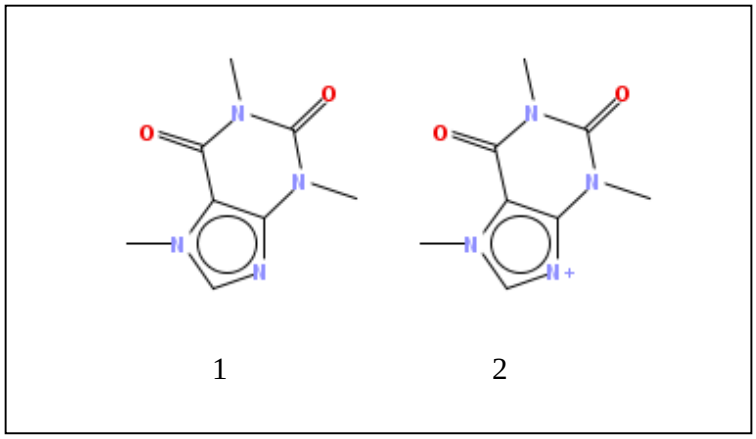


Figure 3: Caffeine Species (Hilal et al. 2011)

Coffee and tea pulps are rich in carbohydrates, proteins, and other nutritional compounds but the anti-nutritional factors such as caffeine and tannins prohibit the pulps to be used as animal feed. In some countries outside of the U.S., pulps generated during tea and coffee processing are generally dumped in the soil then later discharged into nearby water sources. This is a major cause of pollution in water bodies near tea and coffee industries (Gokulakrishnan et al. 2005).

EPI Suite gives an experimental database match of 0.85 for the octanol/water partition coefficient and a solubility of 21,600 mg/L (Appendix C) (US EPA 2011). This suggests that caffeine has the potential to remain in the water phase and if not retained in a drain field, could readily be transported to the water table. The Level III Fugacity

Model estimates that partitioning of caffeine will be predominantly in the soil phase and the remainder in the water phase (Appendix D).

The SPARC on-line calculator gives an estimated pKa of 0.5 for caffeine and the two species shown in Figure 3 (Hilal et al. 2011).

SPARC can also generate a speciation plot that estimates the species fraction versus pH as shown in Figure 4.

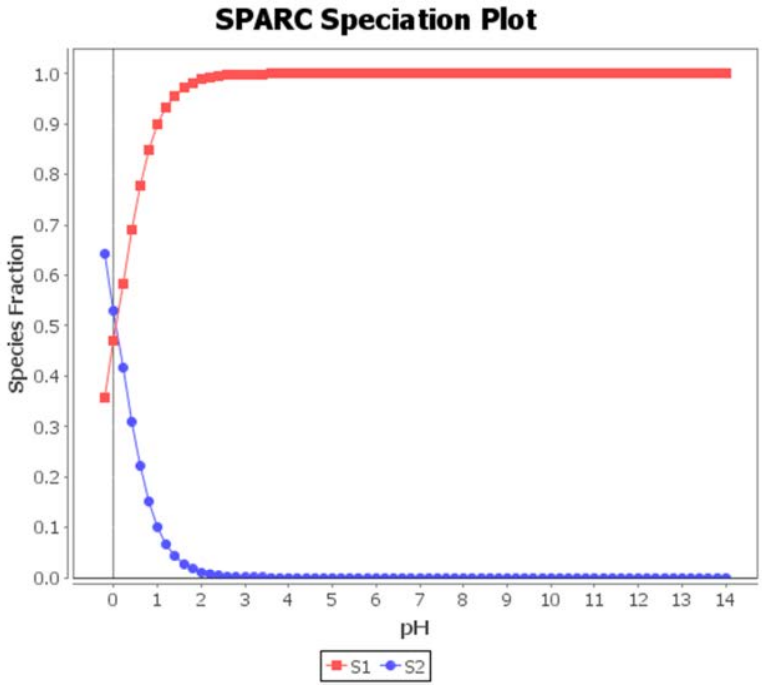


Figure 4: Speciation Plot for Caffeine (Hilal et al. 2011). Refer to Figure 3 for S1 and S2 species.

The speciation plot in Figure 4 suggests that at a pH higher than 2, caffeine will almost be completely present as the neutral species. Therefore in both the septic tank with its pH of almost 7 and in the soil used in this study with a pH of 8, caffeine should be in its neutral form. The Sewage Treatment Plant Model estimates that only 1.9% of caffeine will be removed, which is attributed mainly (1.8%) to biodegradation (Appendix

D). This suggests that although caffeine removal via sorption may be minimal, caffeine may be reduced in an on-site drainfield via biodegradation.

Acetaminophen

Acetaminophen is a widely used (in over 600 brand name drugs) analgesic to relieve mild to moderate pain from headaches, muscle aches, menstrual periods, colds, sore throats, toothaches, backaches, arthritis, and reactions to vaccinations. It is also used as an antipyretic or fever reducer and works by cooling the body and elevating the pain threshold (NCBI 2011). Over eight billion pills of Tylenol®, the brand name of

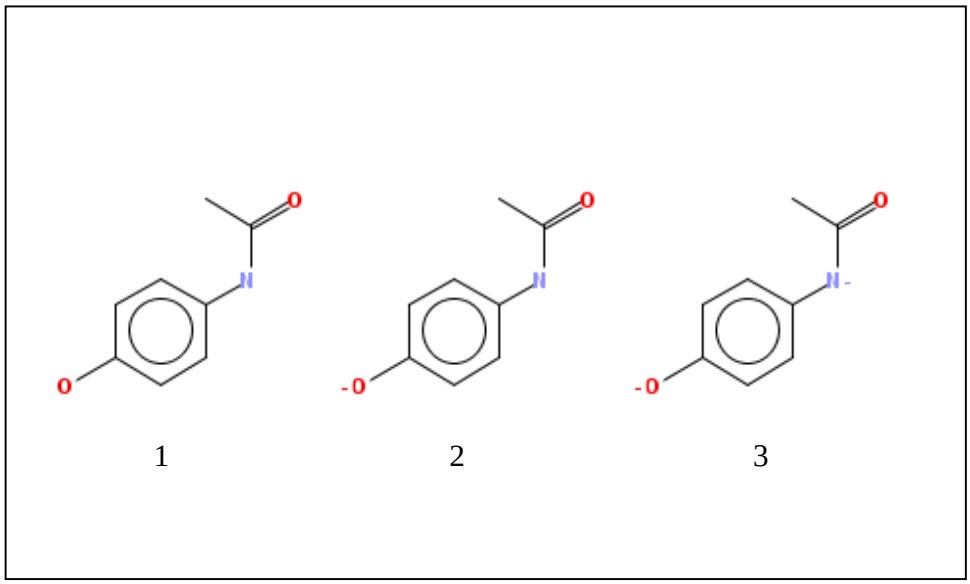


Figure 5: Acetaminophen Species (Hilal et al. 2011)

acetaminophen, are consumed a year in the United States (Seeger Weiss LLP 2010). A maximum daily dose of no more than 4 grams is suggested. Acetaminophen can cause severe hepatoxicity and acute liver failure when taken in large amounts. Under prescribed use, a large amount of the consumed acetaminophen is metabolically conjugated with either a glucuronide or sulfate molecule and expelled in the urine (OSU

College of Pharmacy 2007). In 1999-2000 The U.S. Geological Survey performed a study to provide the first nationwide reconnaissance of the occurrence of pharmaceuticals, hormones, and other organic wastewater contaminants. The results found that over 80% of the 139 streams surveyed were positive for organic wastewater contaminants including acetaminophen (Kolpin et al. 2002).

Acetaminophen is a white, odorless, slightly bitter crystalline powder, has a 1 in 70 solubility in water, is soluble in solutions of alkali hydroxides, and a saturated solution has a pH of about 6 (El-Obeid and Al-Badr 1985).

Acetaminophen is rapidly absorbed after being administered orally and obtains peak levels within 40 to 60 minutes. Metabolites of acetaminophen along with unchanged acetaminophen are excreted by the kidney. After a usual dose of acetaminophen has been administered, 1-4% of the drug will be excreted unchanged, but mainly in the feces with the exception of overdose where up to 10-14% of unchanged acetaminophen is excreted in urine (El-Obeid and Al-Badr 1985). Acetaminophen has a half-life in humans of 2-4 hours. People with hepatotoxicity exhibit a drug half-life greater than the expected 2-4 hours. Approximately 25% of a usual dose of acetaminophen is metabolized during the first pass through the liver. In therapeutic doses the drug is excreted mainly in the urine as various conjugates such as glucuronide conjugates, sulfate, and cysteine and mercapturic acid conjugates (El-Obeid and Al-Badr 1985).

EPI Suite gives an experimental database match of 2.88 for the octanol/water partition coefficient and a solubility of 14,000 mg/L (Appendix C) (US EPA 2011). This suggests that acetaminophen has the potential of remaining mainly in the water phase and

could readily be transferred to the water table if not degraded or removed. The Level III Fugacity model suggests that partitioning of acetaminophen will approximately be between the dominant soil phase and the water phase (Appendix D).

The SPARC on-line calculator gives a pKa of 9.48 for acetaminophen and the following three species shown in Figure 5 and a Speciation plot shown in Figure 6 (Hilal et al. 2011).

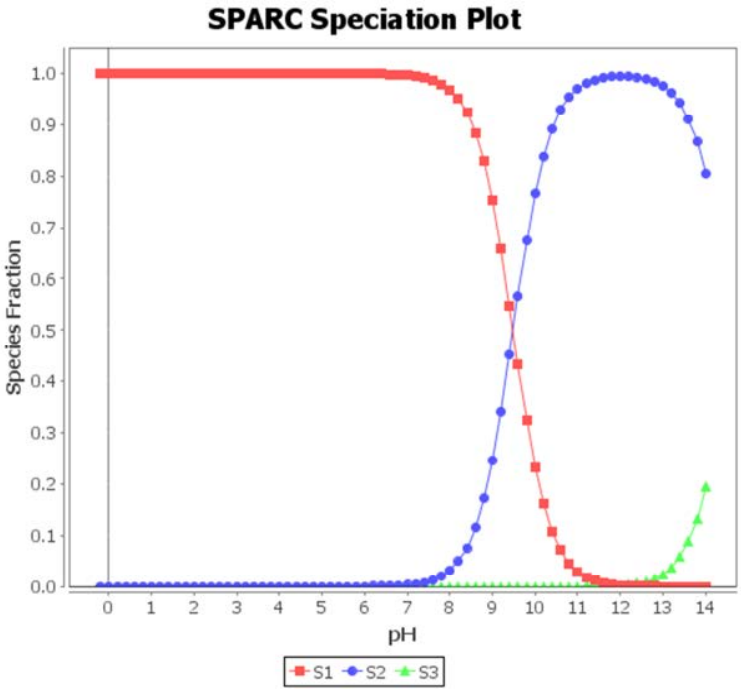


Figure 6: Speciation Plot for Acetaminophen (Hilal et al. 2011). Refer to Figure 5 for S1, S2, and S3 species.

The speciation plot in figure 6 suggests that at the pH of 7 in the septic tank or pH of 8 in the study soil, acetaminophen should be mainly in the Species 1 form, which is the neutral species, but has the potential for part of the species fraction to be in the negatively charged form. If the pH were to increase, more of the acetaminophen would be present

as the negatively charged species and would have the potential to more readily move through negatively charged clays in the soil. The Sewage Treatment Plant Model estimates that 75% of acetaminophen will be removed, which is attributed mainly (74%) to biodegradation (Appendix D). This suggests that although acetaminophen removal via sorption may be minimal, acetaminophen concentrations may be reduced in an on-site drainfield via biodegradation.

Carbamazepine

Carbamazepine is an anticonvulsant used to control certain types of seizures and is used to treat trigeminal neuralgia, a pain causing facial nerve condition. It is also used by patients with bipolar I disorder to treat episodes of mania, depression, and other abnormal moods and works by reducing abnormal electrical activity in the brain (NCBI 2009). It is estimated that 3% of un-metabolized carbamazepine passes through the digestive tract, with the majority being expelled with urination (TEVA Pharmaceuticals USA Inc 2011).

Carbamazepine is readily absorbed from the gastrointestinal tract with a peak concentration in serum at about 2.5 hours after a dose and a half-life between 14-29 hours (Aboul-Enein and Al-Badr 1980).

EPI Suite gives an experimental database match of 281.8 for the octanol/water partition coefficient and a solubility of 112 mg/L (Appendix C) (US EPA 2011). This suggests that carbamazepine has the potential to remain partially in the water phase and partially in the soil phase. The Level III Fugacity model suggests that most of carbamazepine will partition to the soil phase and the remainder in the water phase (Appendix D).

Carbamazepine is a base with a pKa value of 2.3 (Nghiem et al. 2005). The SPARC on-line calculator does not have a plot for carbamazepine but with pH values near 7 and 8 in the septic tank and soil respectively, carbamazepine should be in the uncharged or neutral species form. The Sewage Treatment Plant Model in EPI Suite estimates that the majority of removed carbamazepine will be attributed to biodegradation (Appendix D). This suggests that there may be some biodegradation but even less sorption that could potentially take place in a drain field and that carbamazepine has high potential to end up in the groundwater.

Sulfamethoxazole

Sulfamethoxazole is an anti-bacterial sulfonamide that prevents bacteria from forming dihydrofolic acid, which is vital for their survival. Due to bacterial resistance, sulfamethoxazole is primarily used in conjunction with trimethoprim. It is used to treat malaria, conjunctivitis, toxoplasmosis, and urinary tract infections (Ogbru and Marks 2011).

Sulfamethoxazole is a white to slightly off-white, crystalline powder that is practically odorless. Approximately 50% of excreted sulfamethoxazole is as the metabolite N^4-acetylsulfamthoxazole and only 10% is as the unchanged compound (Goebel et al. 2004).

EPI Suite gives an experimental database match of 7.76 for the octanol/water partition coefficient and a solubility of 610 mg/L (Appendix C) (US EPA 2011). The Level III Fugacity model estimates that most of sulfamethoxazole will be in the soil phase and that remainder will be in the water phase (Appendix D).

Sulfamethoxazole has a cationic, neutral, and anionic species with pKa values of 1.7 and 5.7 (Nghiem et al. 2005). The following Figure 7 shows the speciation of sulfamethoxazole as a function of pH and the three species structures associated with it.

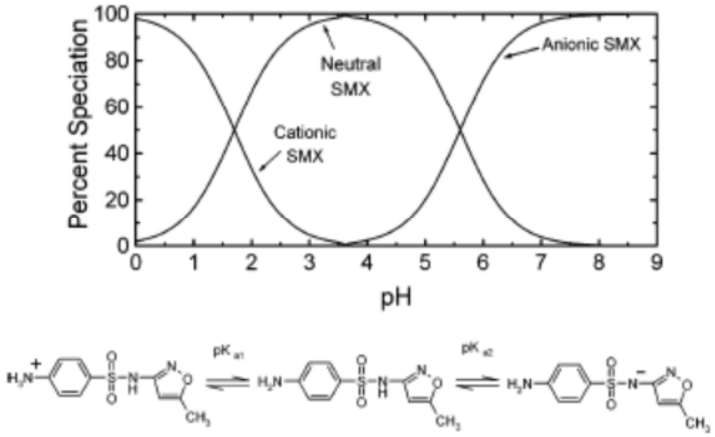


Figure 7: Speciation of Sulfamethoxazole (Nghiem et al. 2005)

Figure 7 suggests that sulfamethoxazole will be mainly in the anionic form when in the septic tank and/or in the soil, and will be more mobile in the soil and less likely to sorb. The Sewage Treatment Plant model also suggests that sulfamethoxazole is less likely to sorb in that the 20% of 22% of its removal in an activated sludge treatment plant would be due to biodegradation (Appendix D).

Progesterone

Progesterone is the principal progestational female hormone made in the ovary and by the placenta. Progesterone prepares the uterine lining to receive and sustain a fertilized egg and thus permits pregnancy. Progesterone can also refer to the synthetic version of the hormone (MedicineNet, Inc. 2011). Progesterone is used as part of

hormone replacement therapy in women who have passed menopause and have not had the uterus removed. Progesterone helps prevent abnormal thickening of the uterine lining, a possible side effect of estrogen incorporated hormone replacement therapy; and therefore can decrease the risk of developing uterine cancer. Progesterone is also used to induce menstruation in childbearing-aged women who have had normal periods and then have stopped menstruating (NCBI 2008).

Progesterone binds to estrogen and progesterone receptors and targets cells in the female reproductive tract, mammary gland, hypothalamus, and the pituitary. Once bound to the receptor, progesterone slows the frequency of gonadotropin-releasing hormone. Progesterone relaxes uterine smooth muscle and stimulates mammary alveolar tissue growth. Absorption of progesterone is prolonged, having an absorption half-life of approximately 25-50 hours (Knox et al. 2011).

Glucuronide and sulfate conjugates of pregnanolone and pregnanediol are excreted in the bile and urine. Progesterone metabolites that are excreted in the bile may undergo enterohepatic recycling or may be excreted in the feces but metabolites are mainly excreted by the kidneys (Knox et al. 2011).

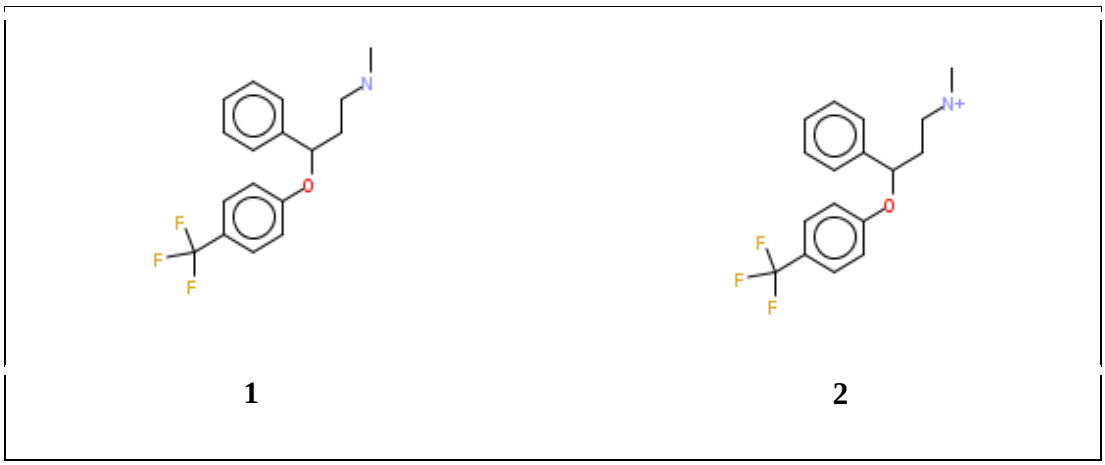
EPI Suite gives an experimental database match of 7,413 for the octanol/water partition coefficient and a solubility of 8.81 mg/L (Appendix C) (US EPA 2011). The Level III Fugacity model suggests that progesterone will predominantly remain in the soil phase with a smaller portion remaining in the water phase (Appendix D). Progesterone has no pKa and remains as a neutral species. The Sewage Treatment Plant model estimates that the 40% total progesterone removal in an activated sludge treatment plant would be due to sludge sorption (22%) and biodegradation (18%) (Appendix D).

This suggests that in a drainfield there may be potential for both biodegradation and sorption of progesterone.

Fluoxetine

Fluoxetine (commonly known as Prozac®) is an antidepressant used to treat depression, obsessive-compulsive disorder, panic attacks, and some eating disorders and can be used to relieve symptoms of premenstrual dysphoric disorder. Fluoxetine is part of a class of selective serotonin reuptake inhibitors that increase the amount of serotonin in the brain in order to help maintain mental balance (NCBI 2011). Side effect in humans can include nausea, nervousness, insomnia, headache, tremor, anxiety, and drowsiness. Fluoxetine is a white to off-white, odorless, crystalline powder that is freely soluble in methanol and ethanol but is insoluble in toluene, cyclohexane, and hexane. A maximum solubility of fluoxetine obtained in water is 14 mg/mL (Risley and Bopp 1990).

Fluoxetine is completely and readily absorbed in the human gastrointestinal



1 **2**

Figure 8: Fluoxetine Species (Hilal et al. 2011)

tract with peak serum levels 6-8 hours after capsule oral dosing. Unchanged fluoxetine and its major metabolite, norfluoxetine, are distributed predominantly in the lung tissue and gradually released. Other fluoxetine metabolites include p-trifluoromethylphenol by O-dealkylation and glucuronides of both fluoxetine and norfluoxetine (Risley and Bopp 1990). Elimination half-life of unchanged fluoxetine is 2-3 days and 7-9 days for norfluoxetine. Maximum drug effect in the central nervous system has been shown to be 8-10 hours after dosing. Metabolism in the liver occurs by N-demethylation. Dosing with C-14 labeled fluoxetine gave a 60% of the activity being recovered in the urine over a 5 week period. 2.5-5.0% was recovered as unchanged fluoxetine, 10% as norfluoxetine, 5.2% as fluoxetine glucuronide, and 9.5% as norfluoxetine glucuronide. An additional 16% of the radio-labeled material was recovered in the feces (Risley and Bopp 1990).

EPI Suite gives an experimental database match of 11,220 for the octanol/water partition coefficient and a solubility of 61 mg/L (Appendix C) (US EPA 2011). The Level III Fugacity model predicts that most of fluoxetine will partition to the soil (Appendix D).

The SPARC on-line calculator gives a pKa of 9.53 for fluoxetine and the following two species shown in Figure 8 and a Speciation plot shown Figure 9 (Hilal et al. 2011).

Figure 9 suggests that in the septic tank (pH 7) and in the study soil (pH 8), fluoxetine should be mainly in the Species 2 form, which is the positively charged species, but has the potential for part of the species fraction to be in the neutral form, especially if the pH were to increase. This also suggests that the positively charged

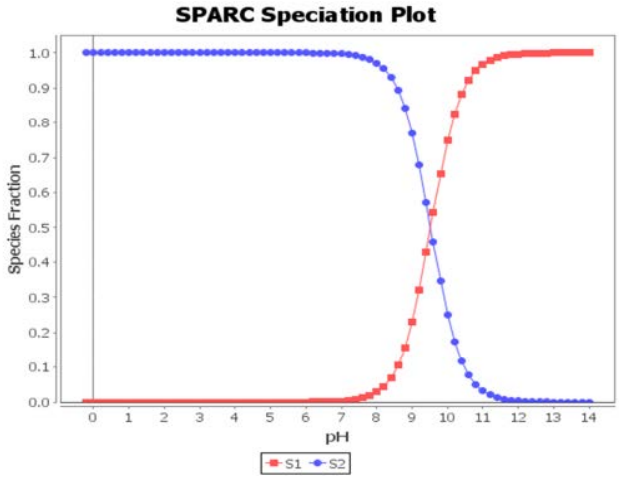


Figure 9: Speciation Plot for Fluoxetine (Hilal et al. 2011). Refer to Figure 8 for S1 and S2 species.

fluoxetine has the potential to sorb to the negatively charged clays in soil and be less mobile towards groundwater. The estimated removal of fluoxetine in an activated sludge sewage treatment plant is almost equally due to sorption as it is to biodegradation (Appendix D). This confirms that fluoxetine would have the potential to both sorb and/or biodegrade.

The results of the sewage treatment plant model is summarized in Table 2.

Table 2: EPI Suite Estimated PPCP Removal in a Sewage Treatment Plant using Activated Sludge

PPCP	Estimated Percent Removal	Estimated Removal due to Biodegradation	Estimated Removal due to Sorption
Caffeine	75%	74%	1%
Acetaminophen	75%	74%	1%
Carbamazepine	24%	22%	2%
Sulfamethoxazole	22%	20%	2%
Progesterone	40%	18%	22%
Fluoxetine	38%	17%	20%

These target PPCPs have the potential to persist in the environment after being used and can cause unanticipated exposure to humans and aquatic organisms. It is important to know whether these PPCPs will persist to drinking water sources and/or aquatic environments or if they will be removed or partially removed to lower levels during on-site wastewater treatment.

CHAPTER IV

STUDY OBJECTIVES AND HYPOTHESIS

1. Better understand the fate of the target PPCPs by determining the percent removal of the target PPCPs in a laboratory scale controlled, conventional, on- site wastewater drain field.
2. Better understand the fate of the target PPCPs by determining the percent removal of the target PPCPs in laboratory controlled drain fields engineered with sorptive media (peat or charred straw) below the gravel layer.
3. Assess if the media used in the engineered drain fields better enhances PPCP removal over the conventional drain field design.
4. Assess the major mechanisms (sorption, biodegradation, or volatilization/hydrolysis) for target PPCP removal in the conventional drain field and the engineered drain fields by comparing PPCP spiked wastewater reactors to PPCP spiked wastewater reactors with inhibited cell activity.
5. Where sorption is a major mechanism for PPCP removal, develop sorption isotherms that could be used to define the amounts of media required for future design of septic system drain fields using the added media.

Based on previous fate studies and models, it is hypothesized that all of the target compounds will have some degree of removal, if only partial, in both a standard on-site wastewater drainfield and in the engineered drainfields. It is assumed that the predominant means of removal will be biodegradation, sorption, or a combination of the two, and that due to the Henry's constants for the compounds (Table 1), volatilization

will be minimal. It is hypothesized that out of the target compounds, caffeine and acetaminophen will have the largest percent removal, due mainly to biodegradation, followed by progesterone and fluoxetine in which percent removal will be attributed to a combination of sorption and biodegradation. The lowest percent removed compounds will be carbamazepine and sulfamethoxazole, for which the low removal will be attributed to biodegradation or a lack thereof.

CHAPTER V

APPROACH

Three experiments were designed to help understand what happens to PPCPs when introduced into a conventional septic system drainfield and into an engineered drainfield. The first experiment was an isotherm study designed to help in understanding the sorptive properties of the media (peat, charred straw, and soil) to be used for future drain field design. The second experiment was designed to investigate the mechanisms of PPCP removal, specifically, if removal can be attributed to sorption, degradation, or volatilization/hydrolysis. The third experiment was column study designed to simulate a septic system drainfield and engineered drainfield, and to estimate an overall percent removal of PPCPs.

Analytical Methods

PPCP concentration was measured using an Agilent Technologies 1200 Series HPLC equipped with an analytical guard column (XDB-C18, 4.6 x 50 mm, 1.8 µm) coupled to an Agilent 6220 Accurate-Mass Time of Flight liquid chromatography/mass spectroscopy (TOF-LC/MS) equipped with a dual chamber ESI. Double deionized water (DDW) with 0.1% formic acid (v/v) as mobile phase A and 90/10 Optima Grade (Fisher Scientific) Acetonitrile to DDW with 0.1% formic acid (v/v) as mobile phase B were used as binary gradient with flow rate of 0.35 mL/min. Twenty microliters of sample were injected and eluted out of the column within 15 minutes. For measurement, an elution program started with 15% of mobile phase B and increased to 100% from 0-5 minutes, remained at 100% from 5-10 minutes, decreased to 15% from 10-12 minutes,

and then continued at 15% during the 5 minute post time. The analysis was performed in positive ion polarity mode for all of the target analytes. External standards of 20 ng/mL, 50 ng/mL, 100 ng/mL, 200 ng/mL, and 500 ng/mL were used to quantify the compounds and 100 ng/mL matrix spikes were used as internal standards to report percent recoveries.

Isotherm Study

After the sorption and biodegradation experiment was first performed, an isotherm study was implemented to assess equilibrium constants and sorption isotherms for each of the media with their respective PPCPs. With these isotherms, one can estimate the sorptive capacity of the sorbent being used. Sorption involves the attachment of a material (sorbate, such as PPCP) to sorbent at an available sorption site such as the outer surface, macropores, and micropores. The amount of sorbate that can be taken up by an sorbent is a function of concentration, temperature, and sorbate characteristics such as solubility, structure, and polarity. Generally, the amount of sorbate sorbed is assessed as a function of the concentration at a constant temperature. The resulting function is called an sorption isotherm. Sorption isotherms are developed by either exposing a given amount of sorbate in a fixed volume of liquid to varying amounts of sorbent or by exposing a given amount of sorbent in a fixed volume of liquid to varying amounts of sorbate (Metcalf and Eddy 2004).

The first set of samples contained 25 mL of 10 mM phosphate buffer, 20% b/v of media, and were spiked with the target PPCPs at varying concentrations (10, 20, 50, 100, 200, and 500 µg/L), similar to the experiment performed by Yu et al. (2011). The second sets of samples contained 25 mL of 10 mM phosphate buffer, no media, and were spiked

with the previous concentrations. The last set was a control sample that contained only the 25 mL of 10 mM phosphate buffer to be used as a matrix blank. All samples had 1% NaN_3 added to maintain sterile conditions. All tubes were shaken continuously (120 rpm) in a mechanical shaker in a temperature-controlled room (15°C) for 24 hours. All samples were then centrifuged, filtered (0.2 µm), and analyzed using TOF-LC/MS. The process was performed in triplicate and with each media type (peat, charred straw, soil). After the experiment was performed, analysis showed that some of the compounds were below their method detection limits, thus not generating enough data to create an sorption isotherm. The experiment using charred straw was repeated but with starting concentrations of 500 and 1000 ng/mL with 20% b/v of charred straw, and with 600, 700, and 800 ng/mL with 10% b/v of charred straw. Peat experiments were repeated with the same amount of media (20% b/v) but at concentrations of 500 and 600 ng/mL. Soil experiments were also repeated with the same amount of media as before (20% b/v) but at concentrations of 500, 600, 700, and 800 ng/mL. Concentrations of 600 and 800 ng/mL were added to the control experiment.

Sorption and Biodegradation Experiment

The column study experiment provided an estimate of potential PPCP percent removal in standard and engineered on-site wastewater drainfields but does not elucidate the mechanisms of removal. The sorption and biodegradation experiment, a modified design of an experiment performed by Yu et al. (2011), was designed to investigate removal mechanisms that may occur in the charred straw, peat, and soil during the PPCP treatment. The removal mechanisms for PPCPs in a bio-treatment system are considered to be biodegradation, sorption, volatilization, and hydrolysis (Yu et al. 2011). In a

temperature controlled room (15°C), nine 1 liter batch reactors were simultaneously running one of three processes designated as Process I, Process II, and Control, as described in Figure 10. Process I was designed to explore possible removal mechanisms (biodegradation, sorption, and volatilization/hydrolysis) occurring in the batch reactors. Process II was designed to investigate sorption and volatilization/hydrolysis by inhibiting cell activity and minimizing biodegradation by using 1% sodium azide (NaN_3). The Control was designed to investigate volatilization/hydrolysis. Yu et al. proposed that the fractional removal credited to biodegradation could be estimated by mass balance of experimental results from Process I subtracted by mass balance of experimental results from Process II. Sorption would then be assessed by mass balance results of Process II subtracted by mass balance results of the Control and mass balance results in the Control were attributed to volatilization/hydrolysis. This assumption, however, has several concerns: 1) sorption capacity may be different between inhibited and uninhibited cells, 2) intermediate products may occupy sorption sites and decrease sorption capacity, 3) the addition of NaN_3 may exhibit competitive sorption behavior (Yu et al. 2011).

Triplicate data was averaged and checked for deviation significance via t-tests and was graphed to determine trends and reaction rates. These graphs and rates were used to estimate mass balances.

All reactors were amber glass bottles so as to minimize photolysis. Initially, for Process I and Process II, 20% by volume (b/v) of media (peat, charred straw, or soil) was placed in each reactor and the reactor filled to 1 liter with 10 mM phosphate buffer. Three different sets of controls were investigated. The first set of controls contained no media and was filled to 1 liter with DDW with 1% NaN_3. The second set of controls did

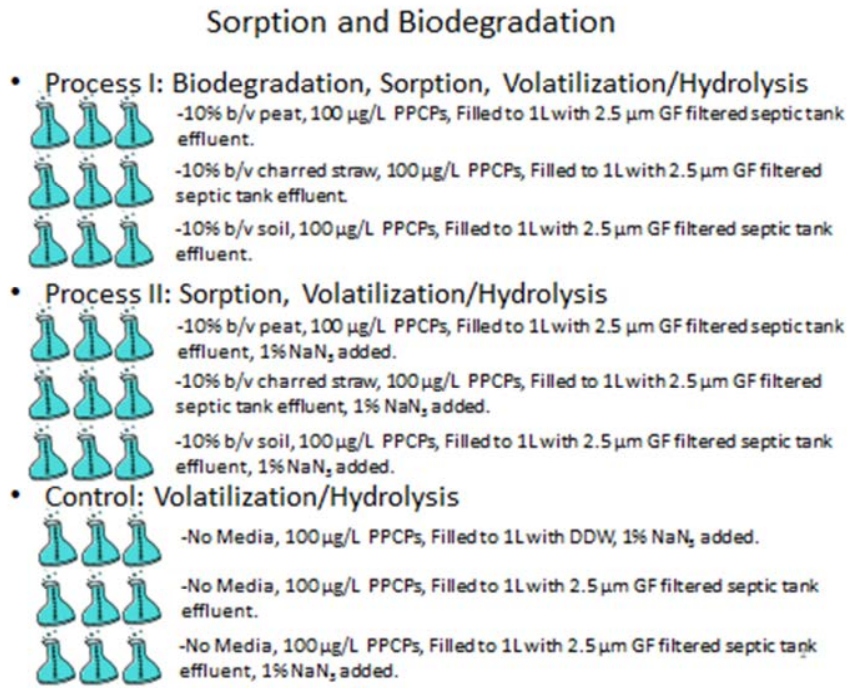


Figure 10: Sorption and Biodegradation Experiment

not contain media and was filled to 1 liter with septic tank effluent that had been filtered using a 2.5 µm glass fiber filter. The third set of controls was the same as the second set except that it also contained 1% NaN_3. The reactors were then spiked to a target initial concentration of 100 ng/mL of each pharmaceutical, then sampling occurred. Results returned poor recoveries partially due to instrument error but did suggest that reduction equilibrium was rapid (within 24 hours) and mainly due to sorption.

The experiment was then repeated but with different amounts of media (5% b/v charred straw, 10% b/v Peat, 20% b/v soil) in order to slow PPCP removal to a more quantifiable time and decrease the percent removal due to sorption. Also, filtered (2.5 µm glass fiber) septic tank effluent was used in the batch reactors instead of the 10 mM phosphate buffer. This was to more closely match biological conditions in a septic system drainfield.

Sampling occurred three times a day during Days 1 and 2, then once a day on Days 3 and 4. Triplicate reactors were used for each media and process, and were sampled in triplicate. At sampling times, 1.5 mL aliquot of liquid sample was taken from each reactor using borosilicate glass pipettes, centrifuged at 11,000 rpm for 5 minutes using an Eppendorf Centrifuge model 5804, and then 1 mL of supernatant was filtered through a 0.2 µm cellulose acetate syringe filter. Loss of analytes to the filters was insignificant. Each sample was spiked with 5 µL of 50 µg/µL Atrazine D5 and 2 µL of 200 ng/µL C-13 caffeine and Acetanilide internal standards, then stored at 4°C for later analysis by TOF-LC/MS.

After the last sampling, desorption experiments were performed with the reactors used for Process II. The reactors were filtered to remove the liquid and air-dried for six days. The reactors were then refilled with the 10mM phosphate buffer solution with 1% NaN_3 (to minimize biodegradation) and thoroughly mixed. The reactors were then sampled every 12 hours for 2 days.

Column Study Experiment

A column study was used to simulate a conventional on-site wastewater drain field and drainfields with added sorptive materials. Nine columns made of two 3 feet long, 6 inch diameter glass segments were used. The columns were open to the air at the top and capped with a sampling port on the bottom. Soil used throughout the column was a Rick's gravelly loam (NRCS 2008) collected from the subsurface of the soil series. The soil was compacted to approximately 94 lbs/ft^3 (bulk density of 1.5 g/cm^3) and was obtained from Utah State University's nearby Huntsman On-Site Wastewater Treatment Training and Demonstration Site at depths of 1-3 feet below grade. Samples of soil used

were analyzed by the Utah State University Analytical Laboratories for physical and chemical properties (Appendix B). The bottom 3 feet of the column was comprised of the sandy loam/loamy sand subsurface soil and is referred to as the unsaturated or vadose zone. The 3 feet of unsaturated soil represents the area directly below the drain field trench and meets the minimal 24 inches of soil required between the bottom of the absorption trench and the water table (The Department of Administrative Rules 2011). A SOILMOISTURE 1908D2.5L Micro Sampler (lysimeter) was placed 12 inches below the bottom of the trench, in the vadose zone in six of the nine columns (two for each media type). The sorption media and 4 inch diameter perforated pipe were then placed above the vadose zone to meet R317-4 specifications.

In the control columns representing conventional drainfields, the media was comprised only of ¾ inch gravel and was filled to 6 inches above the saturated zone, then 4 inches surrounding the 4 inches diameter perforated pipe, then another 2 inches above the perforated pipe for a total of 12 inches of rock filled above the unsaturated zone. The other six columns were similar in design with the exception that an additional 2 inches of peat or charred straw media (three columns with peat, three columns with charred straw) were placed at the bottom of the ¾ inch gravel layer (compacted to a bulk density of approximately 0.293 g/mL and 0.22 g/mL, respectively). All of the columns had a synthetic filter fabric comprised of GEONET filter fabric placed on top of the ¾ inch gravel layer to prevent backfilled soils from entering the gravel area and filling the gravel voids. The filter fabric was also porous so as to not create a liquid or air barrier. The column was then filled with soil above the filter fabric to the top of the column. Figure 11 provides a graphical description of all three types of columns used in the study.

Analyte concentration reduction via sorption to the tubing used within and without the columns was estimated by continuously passing a known concentration (200 ng/mL) of the target compounds in DDW throughout the tubing for an hour and comparing the change in concentration. Results (Appendix E) showed that changes in concentration for all of the compounds were statistically insignificant with the Teflon tubing (used in conjunction with wastewater collection at the base of the columns) whereas some sorption may take place with the PVC tubing (used in conjunction with pumping the wastewater into the columns) for the pharmaceutical progesterone. This possible sorption may have decreased the amount of progesterone that ended up going into the columns.

Particle density was estimated for soil, peat, and charred straw by placing 100 mL of media (150 g, 29.3 g, and 22 g, respectively) in a graduated cylinder, adding 100 mL of DDW, waiting for the liquid to permeate through the media, and by recording how much the 100 mL of DDW was displaced. For example, 100 mL of DDW was displaced to the 150 mL graduation on the cylinder when poured over 29.3 grams of peat and allowed to permeate. Therefore peat had a particle density of 29.3 grams per 50 mL or 0.586 g/mL. Soil and charred straw had particle densities of 2.3 g/mL and 0.55 g/mL, respectively. Porosity was then estimated by taking 1 minus the bulk density divided by the particle density. It was assessed that the soil, peat, and charred straw had porosities of 35%, 50%, and 60%, respectively.

A bromide tracer test was performed to investigate water movement and retention time in the columns. Tracers are used to help define hydraulic parameters such as conductivity, porosity, and dispersivity. An ideal tracer is non-toxic, moves with the

water, is chemically stable for a desired length of time, is easy to detect in trace amounts, is naturally low in abundance where the tracer is being performed, and does not alter the natural direction of the flow of water (Davis et al. 1980). Bromide was used as a tracer due to its low abundance in nature and low toxicity and cost.

The tracer test was performed by wetting the columns with tap water until liquid dripped out the bottom of the column. Once liquid had begun to drain out the bottom, 9 liters of 50 mg/L sodium bromide (NaBr) tracer was pumped to the columns (1 liter per column). After the 9 liters of tracer had been pumped, tap water was pumped through the columns until the concentration of bromide had peaked then returned to background.

Bromide was measured using an Orion® bromide electrode and an Orion® double-junction reference electrode. Both probes, along with a temperature probe, were connected to an Accumet® XL25 Dual Channel pH/Ion meter operated in millivolt mode. The instrument was calibrated by adding 5 mL of NaBr standard (2.4, 8.0, 80, and 180 mg/L), 10 mL DDW, and 0.3 mL of ionic strength adjustor (5 M $NaNO_3$) to a sample cup, mixing, and taking a millivolt reading.

A standard curve was then plotted as millivolt readings versus log concentrations to show linearity. Liquid was collected from the sampling port at the bottom of the columns every several hours, beginning with the initial wetting of the columns, and measured for bromide. Liquid not sampled was volumetrically measured in order to allow determination of a mass balance.

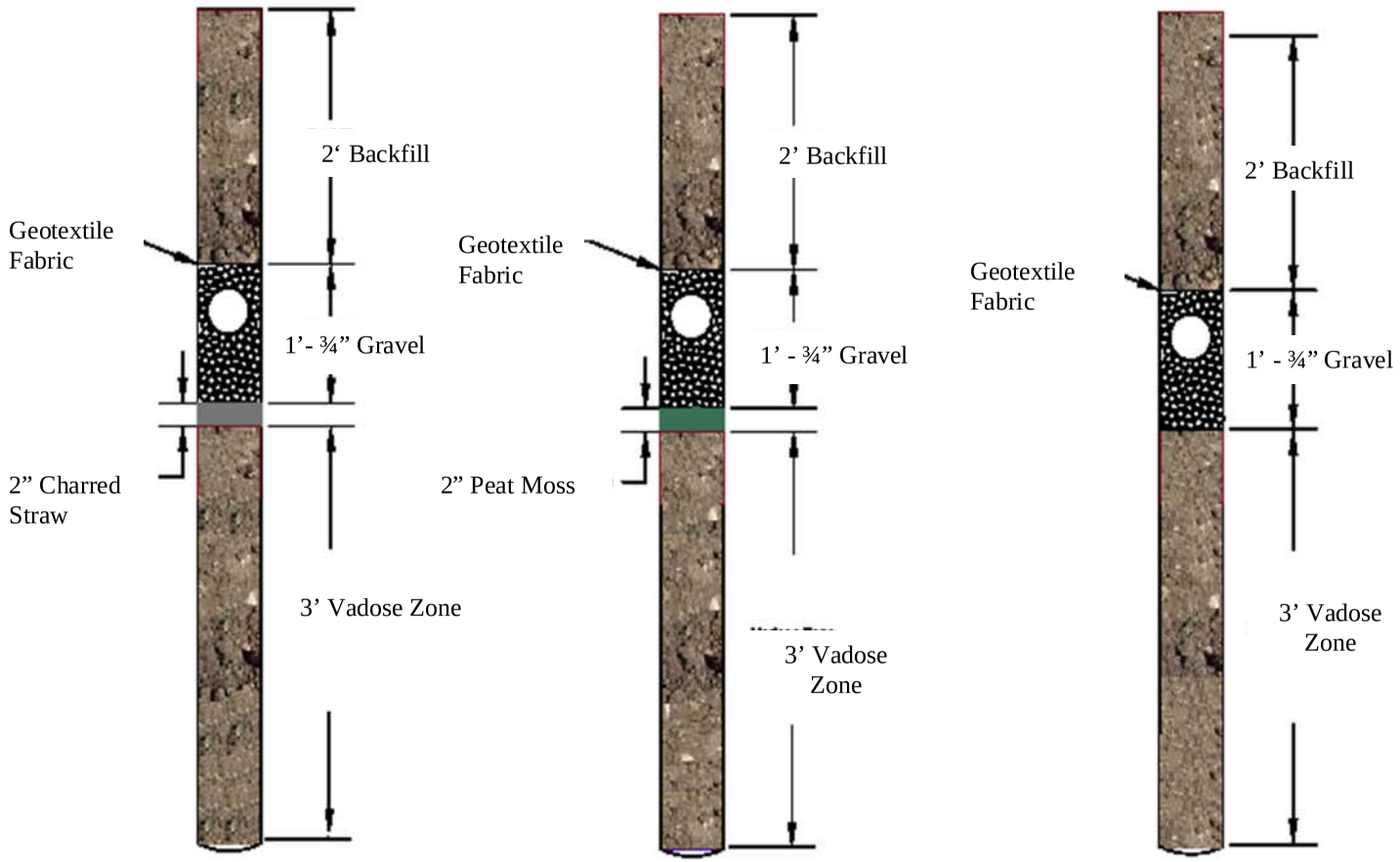


Figure 11: Column Layout

Wastewater used in the study came from the home septic tank of a Utah Water Research Laboratory employee. The wastewater at the effluent end of the septic tank was slightly acidic with a pH of 6.7. A homeowner survey (Appendix F: Homeowner Survey) was conducted to evaluate water habits and usage and possible pharmaceuticals used by household residents.

Wastewater was collected using a Global Water Variable Speed Portable Sample Pump (Model # SP200) from the outlet pipe of the septic tank and stored in 4-L glass amber bottles (that had been previously washed with methanol and rinsed with DDW), and transported back to the laboratory on ice. Once at the laboratory, the 4-L bottles were stored in the refrigerator when not in use. Triplicate samples were taken from each of the 4-L bottles, prior to and after being spiked with PPCPs, and were analyzed to achieve baseline and spiked concentrations for the target compounds: caffeine, acetaminophen, carbamazepine, sulfamethoxazole, progesterone, and fluoxetine. Baseline concentrations indicated that caffeine and acetaminophen were already present in the septic tank. Once a day, two of the 4-L (8 liters total) bottles of wastewater were spiked with 100 ng/mL of the target PPCPs and were pumped into the columns at approximately 8.93 mL/min using a Watson-Marlow 205U auto/manual-control multi-channel pump. A concentration of 100 ng/mL was chosen for ease of analysis, at which represented very high levels of concentrations that might be found in septic tank effluents. Once the wastewater had passed through the columns, the effluent was collected in 1-L glass amber bottles. Liquid samples were also collected from the lysimeters into 10 mL serum vials. Since compounds remaining in the liquid phase are of interest, the samples collected in the 1-L amber bottles (effluent), the baseline samples

(influent), the spiked influent samples (influent w/PPCP), and the samples from the lysimeters (mid-column) were filtered with 0.2 µm polyethersulfone or cellulose acetate syringe filters (filters are hydrophilic so sample loss is minimal) and analyzed directly by TOF-LC/MS. The resulting effluent analyte concentrations were compared to the influent concentrations, and a percent removal was calculated.

Method Detection Limit (MDL)

The method detection limit for each PPCP studied was calculated using the U.S. EPA procedure found in Title 40 Code of Federal Regulations Part 136 (US EPA 2012). The procedure was conducted by estimating the detection limit using concentration values that corresponded to an instrument signal/noise in the range of 2.5 to 5. A concentration of 10 ng/mL was chosen as the estimated detection limit for all of the target compounds. A 10 ng/mL solution of the target PPCPs in DDW was prepared, and 10 aliquots of the solution were processed and analyzed through the analytical method. Method detection limits were assessed by calculating standard deviations for each compound's ten samples and then by multiplying by the students' t-value appropriate for a 99% confidence level with n-1 degrees of freedom (2.821). Calculated method detection limits are presented in Table 3.

Table 3: Method Detection Limits

Compound	MDL (ng/mL)
Acetaminophen	4.5
Caffeine	7.0
Sulfamethoxazole	5.5
Fluoxetine	2.0
Carbamazepine	4.5
Progesterone	2.5

CHAPTER VI

RESULTS AND DISCUSSION

Isotherm Study Results

Results from the isotherm study are tabulated in Appendix G: Isotherm Results. Results below the method detection limit and results whose matrix spike percent recoveries were below 40% or above 160% were eliminated from calculations. With the data, an absorbent phase concentration after equilibrium can be calculated using Equation 1 (Metcalf and Eddy 2004).

Equation 1: Sorption Isotherm

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where q_e = sorbent phase concentration after equilibrium, ng PPCP/g media
C_0 = initial concentration of PPCP, ng/mL
C_e = final equilibrium concentration of PPCP, ng/mL
V = volume of liquid in the reactor, mL
m = mass of media, g

Graphical representations of the sorption isotherms are found in Appendix H: Sorption Isotherms. Equations that are often used to describe the isotherm data include the Freundlich, Langmuir, and Brunauer, Emmet, and Teller (BET) isotherm, with the Freundlich isotherm being the most commonly used in water and wastewater treatment (Metcalf and Eddy 2004). Results from the isotherm study were applied to Freundlich isotherms as well as Langmuir isotherms. The Freundlich isotherm was designated as the best fitting isotherm based on graphical comparisons of the Freundlich isotherm versus the sorption isotherm having slopes and correlation coefficients (R^2) nearest to 1, and the

residuals plot having slopes and correlation coefficients nearest to zero. The linearized form of the Freundlich isotherm is defined in Equation 2 as (Metcalf and Eddy 2004):

Equation 2: Linearized Freundlich Isotherm

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} log C_e$$

where x/m = mass of sorbate sorbed per unit mass of sorbent, ng PPCP/g Media
K_f = Freundlich capacity factor, (ng PPCP/g media)(mL water/ng PPCP)$^{1/n}$
C_e = equilibrium concentration of sorbate in solution after sorption, ng/mL PPCP
1/n = Freundlich intensity parameter

A tabulated version of the Freundlich isotherm, which includes the linear equations for the Freundlich isotherms, Freundlich vs. Sorption Isotherms, residuals and the corresponding correlation coefficients (R^2), is given in Appendix I: Tabulated Freundlich Isotherm. Figure 12 shows the graphical Freundlich isotherms for each of the target PPCPs.

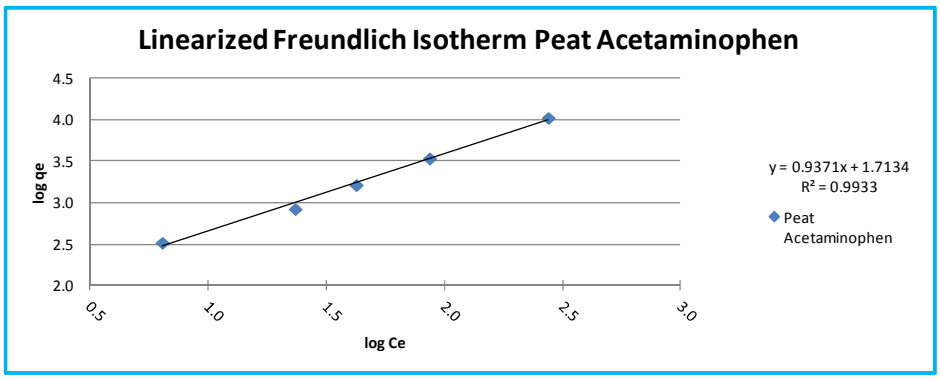


Figure 12: Linear Freundlich Isotherms :

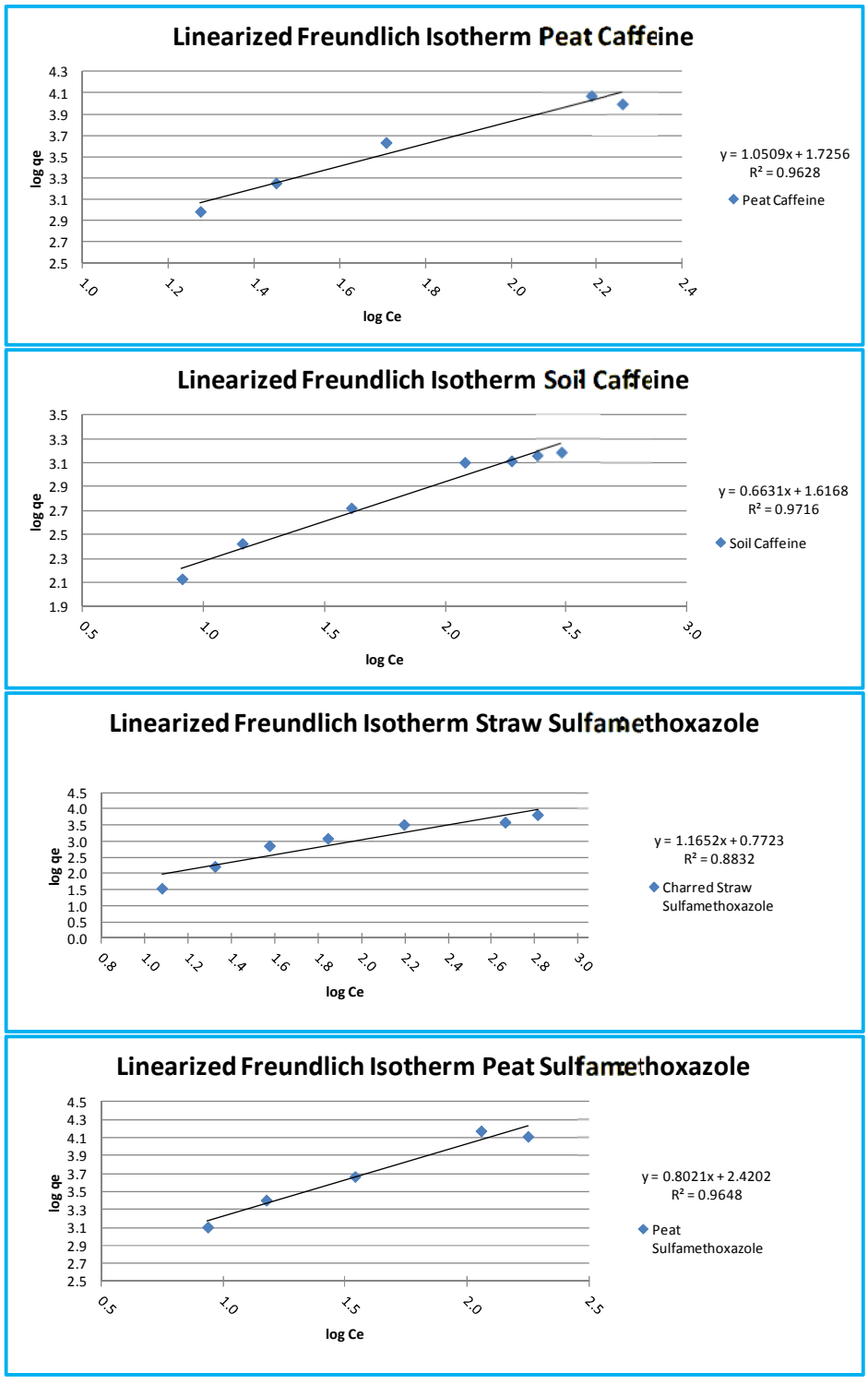


Figure 12 (cont.) Linear Freundlich Isotherms

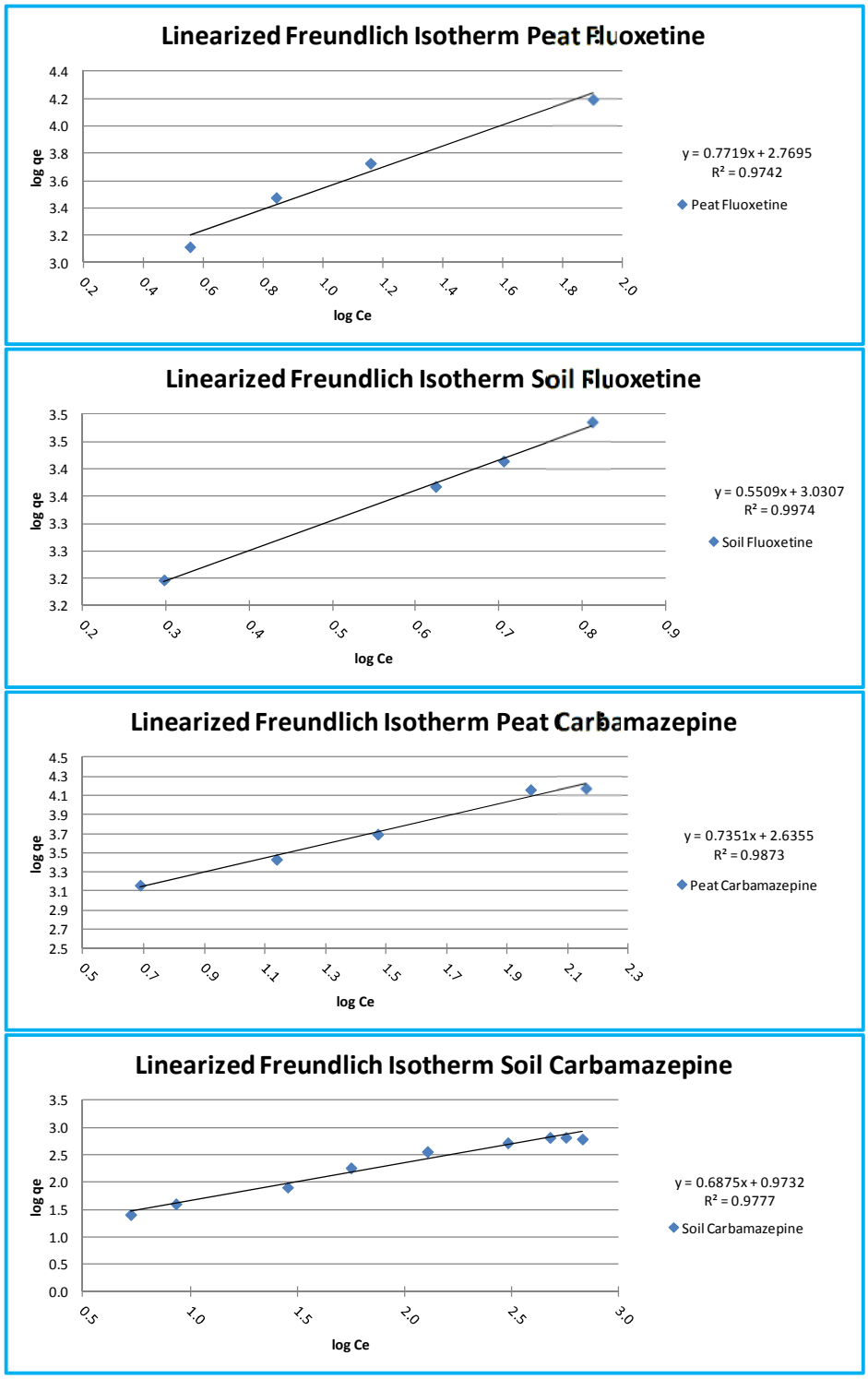


Figure 12 (cont.) Linear Freundlich Isotherms

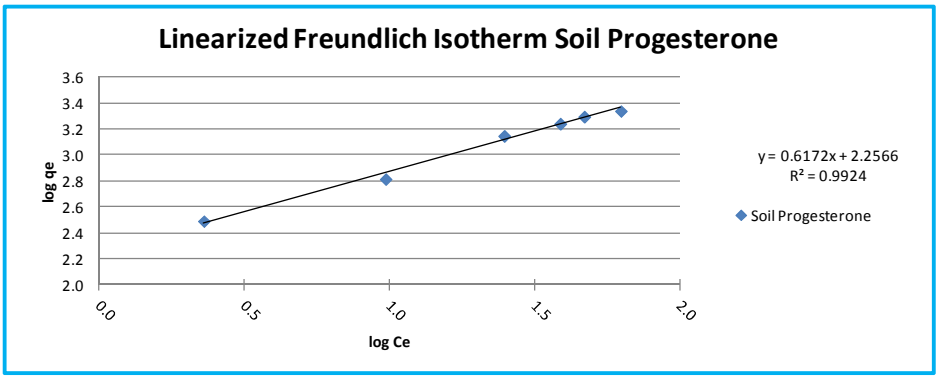


Figure 12 (cont.) Linear Freundlich Isotherms

Desorption

Results from the desorption experiment can be found in Appendix J: Desorption. It should be noted that the experiment returned poor percent recoveries (below 40% or above 160%) of matrix spiked samples, therefore the following conclusions regarding desorption are made with limited confidence.

Desorption of acetaminophen appeared to occur only in the peat batch reactor that had 1% NaN_3 (Process II) added to it and leveled off between 20 and 25 ng/mL. Desorption of caffeine appeared in both the peat and soil batch reactors. Concentrations of caffeine in the peat reactors ranged between 10 and 12 ng/mL whereas concentrations of caffeine ranged between 5 and 10 ng/mL in the soil reactors. Desorbed concentrations of sulfamethoxazole ranged from 4-12 ng/mL, 3-25 ng/mL, and 6-15 ng/mL for the charred straw, peat, and soil batch reactors, respectively. The higher ends of the ranges corresponded to batch reactors where sorption was the primary means of target compound reduction. Desorption of fluoxetine was only seen in peat batch reactors where both degradation and sorption were mechanisms for target compound removal, but

the concentrations were within 2 ng/mL of the method detection limit. Carbamazepine showed a steady increase of desorption in the batch reactors for both Process I and Process II and in peat batch reactors representative of Process I. The peat batch reactors for Process II also indicated desorption but did not increase past 10 ng/mL in the amount of time used for the desorption experiment. Desorption was not quantifiable in the progesterone batch reactors. Desorption also was not quantifiable in the control columns indicating that sorption to the glass bottles was minimal.

Isotherm Study Discussion

Table 4: Sorptive Capacities

Compound	Media	Sorptive Capacity	
Acetaminophen	Soil	NA	ng/g
	Peat	3869.01	ng/g
	Charred Straw	NA	ng/g
Caffeine	Soil	877.00	ng/g
	Peat	6720.48	ng/g
	Charred Straw	NA	ng/g
Sulfamethoxazole	Soil	NA	ng/g
	Peat	10577.91	ng/g
	Charred Straw	1266.78	ng/g
Fluoxetine	Soil	13567.51	ng/g
	Peat	20573.11	ng/g
	Charred Straw	NA	ng/g
Carbamazepine	Soil	222.95	ng/g
	Peat	12755.57	ng/g
	Charred Straw	NA	ng/g
Progesterone	Soil	3097.42	ng/g
	Peat	NA	ng/g
	Charred Straw	NA	ng/g
C_e=100 ng/mL			

NA – Not accurately quantified.

Results indicated that sorption of sulfamethoxazole to soil was too low to quantify, therefore an isotherm plot was not generated for soil with sulfamethoxazole. The linearized Freundlich isotherm plots can be used to estimate the sorptive capacity (Table 4) by extending a vertical line from the point on the horizontal axis corresponding to the initial concentration, and extrapolating the isotherm to intersect this line (Metcalf and Eddy 2004). Isotherms for charred straw with PPCPs (with the exception of sulfamethoxazole) produced poor correlation coefficients, as did soil with acetaminophen and peat with progesterone; therefore isotherms were not generated for these cases. Overall, results indicated that peat had the greater sorptive capacity for the PPCPs.

Results from the control isotherms (Appendix K: Control Isotherms) suggest that some sorption to the polypropylene centrifuge tubes may have occurred with fluoxetine and progesterone, but the remainder of the compounds showed no significant reduction in the controls.

Sorption and Biodegradation Experiment Results

Batch reactor results from the sorption and biodegradation experiment were graphed and are shown in Appendix L: Batch Reactors, with the error bars indicating the 95% confidence interval for the triplicate samples. An example is shown in Figure 13.

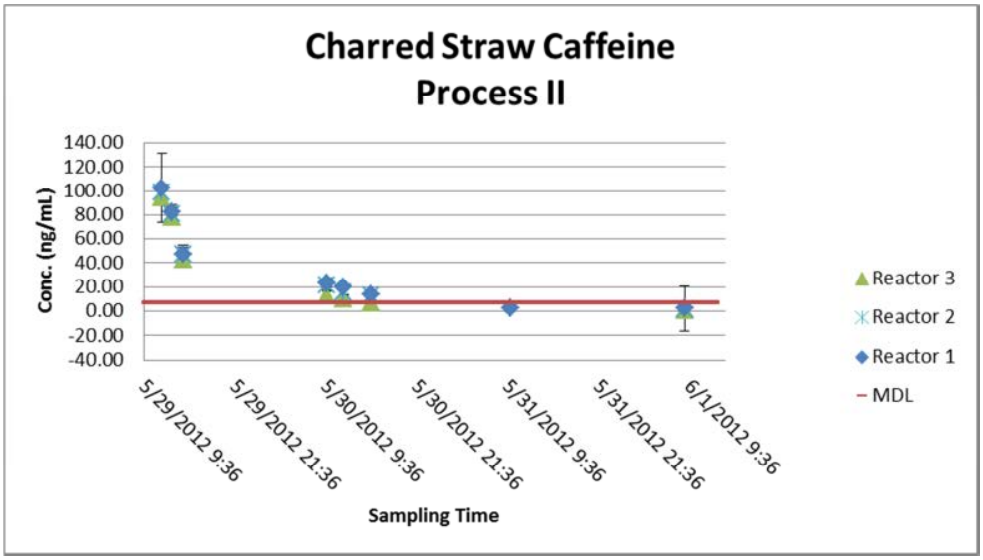


Figure 13: Charred Straw with Caffeine Batch Reactor, Process II

Graphical results from Process II (Appendix L) suggest that sorption occurs relatively quickly (within the first 24 hours). Because of concerns discussed earlier regarding differing sorption masses from sorption/biodegradation masses and because sorption occurs rapidly, PPCP reduction in the batch reactors representing Process I was assumed to follow a 1st order degradation reaction, as shown in Equation 3.

Equation 3: 1st Order Degradation Reaction

$$C = C_0 e^{-k_1 t}$$

where C = final PPCP concentration, ng/mL
C_0 = initial PPCP concentration, ng/mL
k_1 = 1st order reaction constant, d^{-1}
t = sampling time, d

The 1st order reaction constants for each PPCP were ascertained by graphing the natural log of the final concentration over the natural log of the initial concentration, versus the sampling period (Appendix M: 1st Order Graphs). The corresponding slope

equals the 1st order reaction constant. Results below the method detection limit were eliminated from calculations as were results whose matrix spike percent recoveries were below 40% or above 160%. The reaction rates from the triplicate reactors were averaged and tabulated into Table 5.

Table 5: First Order Rate Constants for Process I

Media In Wastewater Matrix	Compound	Sorption/Degradation		
		Rate Constant (k) (d^{-1})	Correlation Coefficient (R^2)	Half Life (d)
Peat	Acetaminophen	0.212	0.726	3.27
Peat	Caffeine	0.321	0.797	2.16
Peat	Sulfamethoxazole	0.382	0.752	1.82
Peat	Fluoxetine	15.210	0.996	0.05
Peat	Carbamazepine	0.323	0.821	2.15
Peat	Progesterone	0.984	0.765	0.70
Charred Straw	Acetaminophen	0.994	0.880	0.70
Charred Straw	Caffeine	2.297	0.911	0.30
Charred Straw	Sulfamethoxazole	0.253	0.564	2.74
Charred Straw	Fluoxetine	20.137	0.965	0.03
Charred Straw	Carbamazepine	0.977	0.917	0.71
Charred Straw	Progesterone	2.617	0.858	0.26
Soil	Acetaminophen	0.697	0.921	0.99
Soil	Caffeine	17.163	0.732	0.04
Soil	Sulfamethoxazole	0.041	0.744	16.90
Soil	Fluoxetine	5.254	0.945	0.13
Soil	Carbamazepine	0.181	0.504	3.82
Soil	Progesterone	32.867	0.915	0.02
No Media	Acetaminophen	0.078	0.335	8.89
No Media	Caffeine	0.064	0.43	10.83
No Media	Sulfamethoxazole	0.023	0.42	30.13
No Media	Fluoxetine	0.102	0.552	6.80
No Media	Carbamazepine	0.061	0.633	11.36
No Media	Progesterone	2.165	0.885	0.32
No Media, NaN_3	Acetaminophen	0.029	0.409	23.90
No Media, NaN_3	Caffeine	0.039	0.365	17.77
No Media, NaN_3	Sulfamethoxazole	0.005	0.101	138.62
No Media, NaN_3	Fluoxetine	0.123	0.692	5.63
No Media, NaN_3	Carbamazepine	0.044	0.621	15.75
No Media, NaN_3	Progesterone	0.109	0.774	6.36

Sorption and Biodegradation Experiment Discussion

A mass balance of both controls in DDW with 1% NaN_3 (Appendix L) and controls in septic tank effluent with 1% NaN_3 (Table 5) did not show significant reduction in PPCP concentration. This suggests that, volatilization/hydrolysis and sorption to the glass containers were minimal, as was hypothesized based on the Henry's Law constants pertaining to each of the compounds. Mass balance of the controls in septic tank effluent without NaN_3 added also showed minimal reduction in concentration with the exception of progesterone. The sorption and biodegradation experiment controls (Appendix L & Table 5), along with results from isotherm study, indicate that sorption is the main mechanism in the target PPCPs' reduction. The low amount (average of 0.6%) of organic matter (i.e., less biological activity to biodegrade PPCPs) in the soil and cation exchange capacity of peat (30 cmol/kg, Appendix B) help support the conclusion that sorption is the main mechanism in PPCP reduction versus biodegradation in the experiment's system.

Progesterone in filtered wastewater and no media had a degradation constant of 2.165 d^{-1} suggesting that biodegradation plays a significant role in the reduction of progesterone. This is also supported by the fact that although charred straw had the greatest sorptive capacity for progesterone, the largest overall sorption/degradation constant was for progesterone with soil. Mass balance indicated that progesterone and fluoxetine were ~100% removed within the first 30 hours for both processes and all three mediums. Caffeine was ~100% removed within the first 30 hours for both processes with charred straw or soil as the media but was only ~60% removed within the first 30 hours with peat as the media. Acetaminophen reached ~100% removal for both processes with the charred straw and soil but not until after 72 hours. Acetaminophen only reached

~50% removal at 72 hours. Carbamazepine reached ~100% removal after 72 hours for both processes with charred straw as the media but only ~50% with the peat or soil as the media. Sulfamethoxazole only reached ~50% removal for both processes with charred straw or peat as the media whereas it only reached ~10% removal with soil as the media.

Caffeine had the largest sorption/degradation rate constant with soil as the media, whereas the largest sorption/degradation constants for acetaminophen, fluoxetine, and carbamazepine were with charred straw. As with the results from the isotherm study, sulfamethoxazole had the greatest sorption/degradation rate constant with peat.

Column Study Experiment Results

Figure 14 shows the results from comparing influent spiked with PPCPs ("Influent") with the concentrations measured at the base of the columns ("Peat Columns Average," etc.). Markers labeled "Control Column" correspond to the columns representing conventional septic system drainfields not engineered with the addition of peat or charred straw.

Two hundred liters of spiked septic tank effluent was pumped to the nine columns over 25 days. The method detection limit (MDL) for sulfamethoxazole was reached on the 10th day of pumping with the control columns and two of the three peat columns. The third peat column reached the MDL 4 days later when two of the charred straw columns also reached the MDL, although the charred straw columns only reached the MDL for two days before dipping below the limit. The percent removal in the control columns peaked at 72% ±0.09% removal of sulfamethoxazole whereas the percent removal in the peat columns peaked at 81% ±0.05% removal. Concentration breakthrough is attained when the effluent concentration is 5% of the influent

concentration and exhaustion is reached when effluent concentration is 95% of the influent concentration (Metcalf and Eddy 2004). Therefore the breakthrough concentration for sulfamethoxazole was at the method detection limit and therefore the control and peat columns reached the breakthrough concentration at day 10 of pumping.

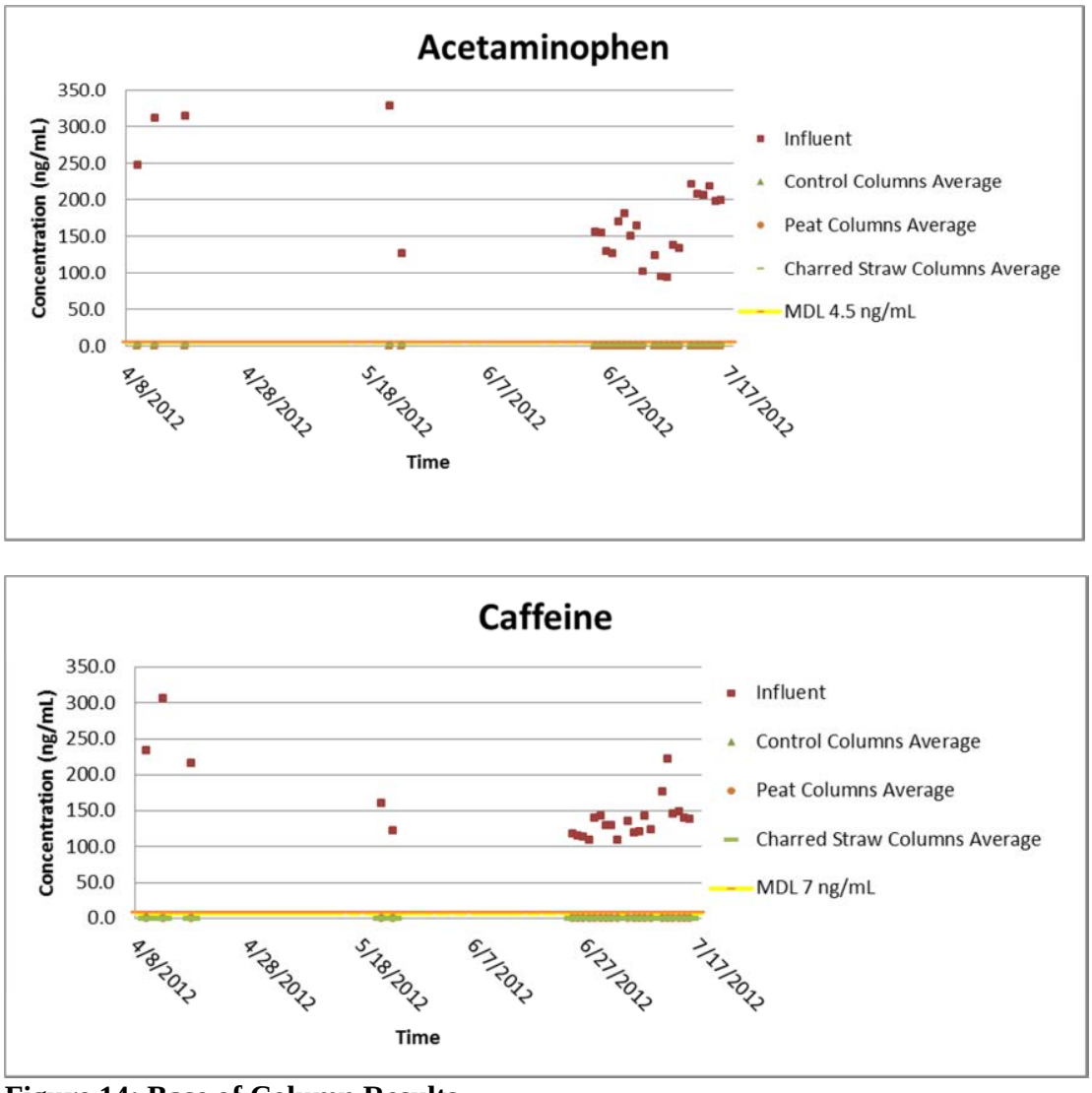
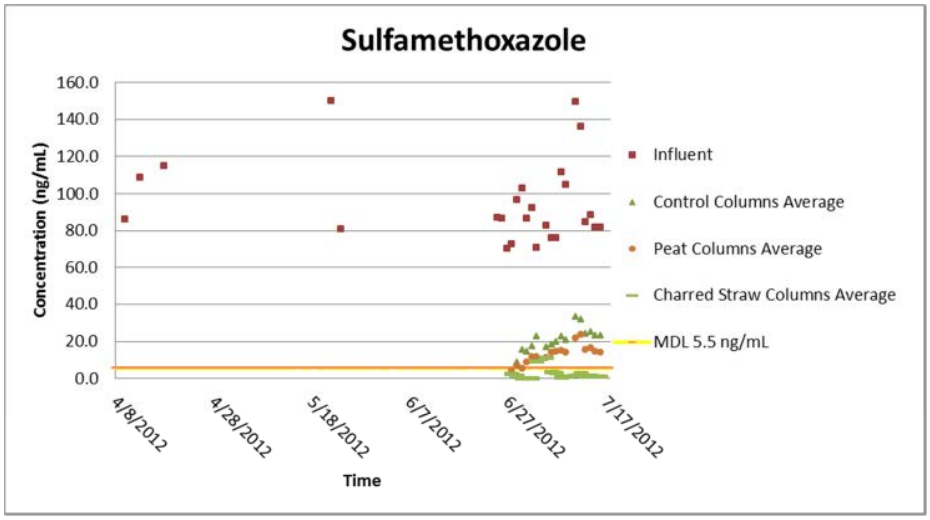
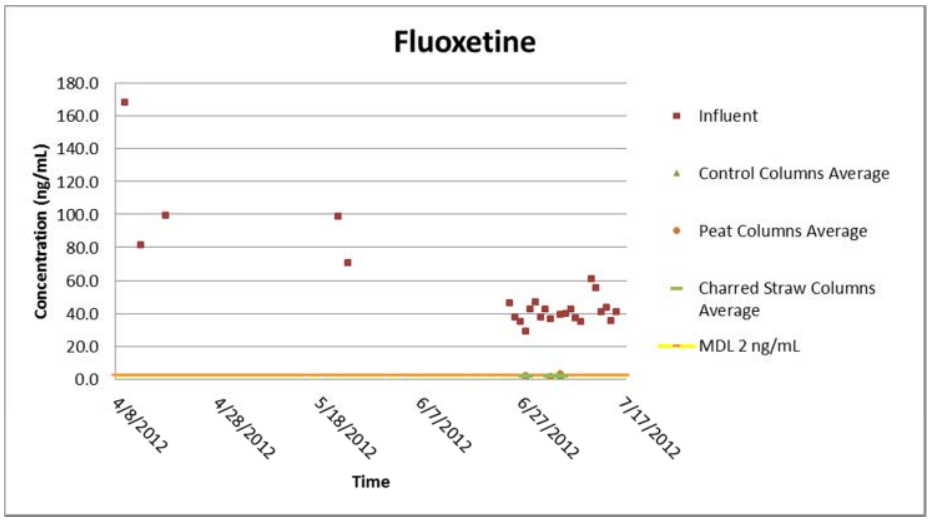


Figure 14: Base of Column Results





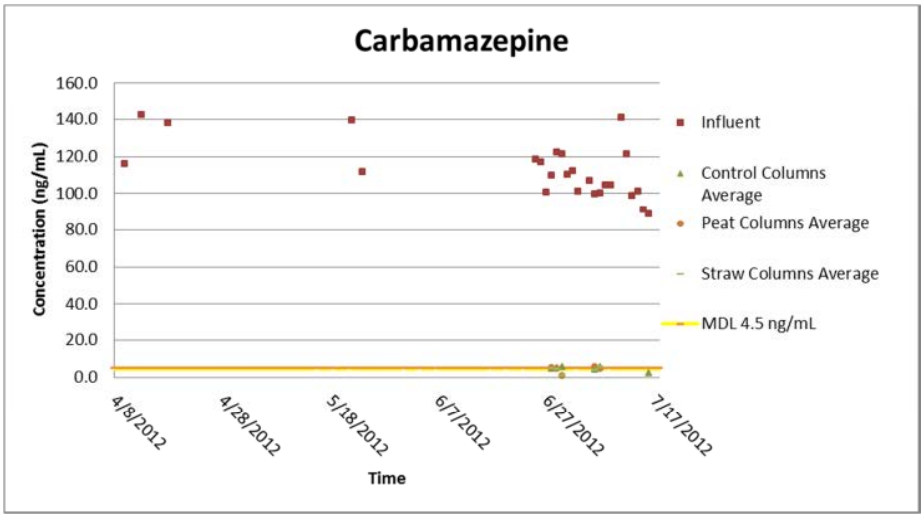


Figure 14 (cont.): Base of Column Results

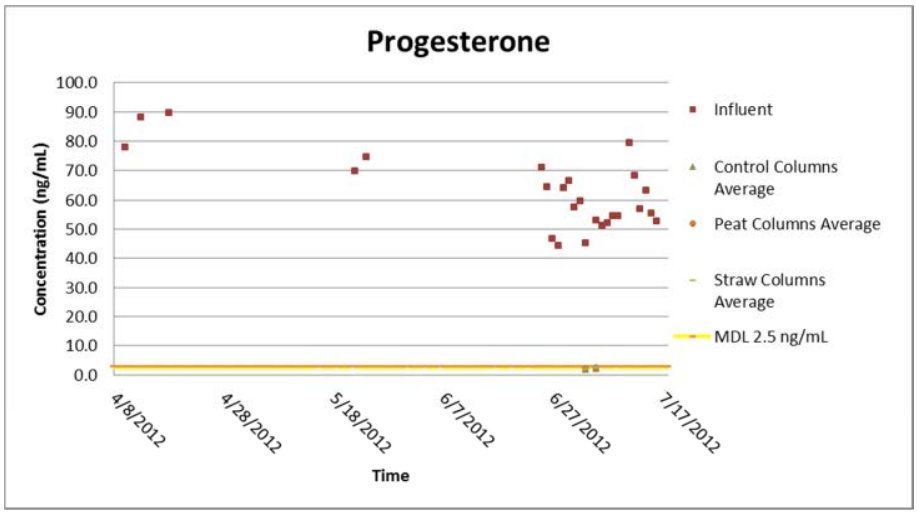


Figure 14 (cont.): Base of Column Results

Carbamazepine stayed near the method detection limit from days 9-11 and days 16 and 17. In both instances the concentrations remained within 2 parts per billion of the method detection limit and therefore were most likely instrument error and not indicators of carbamazepine approaching the breakthrough period. None of the other target PPCPs reached the method detection limit during the time of the experiment nor did the columns reach exhaustion at the bottom sampling ports.

Figure 15 shows the results from water samples collected from the lysimeters placed a foot below the drainfield.

Sampling of the lysimeters did not begin until day 10 of pumping; therefore sulfamethoxazole had already reached breakthrough in the control and peat columns but had presumably just began to reach breakthrough in one out of the two of the charred straw columns. The other charred straw column never reached breakthrough for

sulfamethoxazole during the time of the experiment. Sulfamethoxazole peaked at 35% ± 0.06% reduction in the control columns and 56% ± 0.09% reduction in the peat columns.

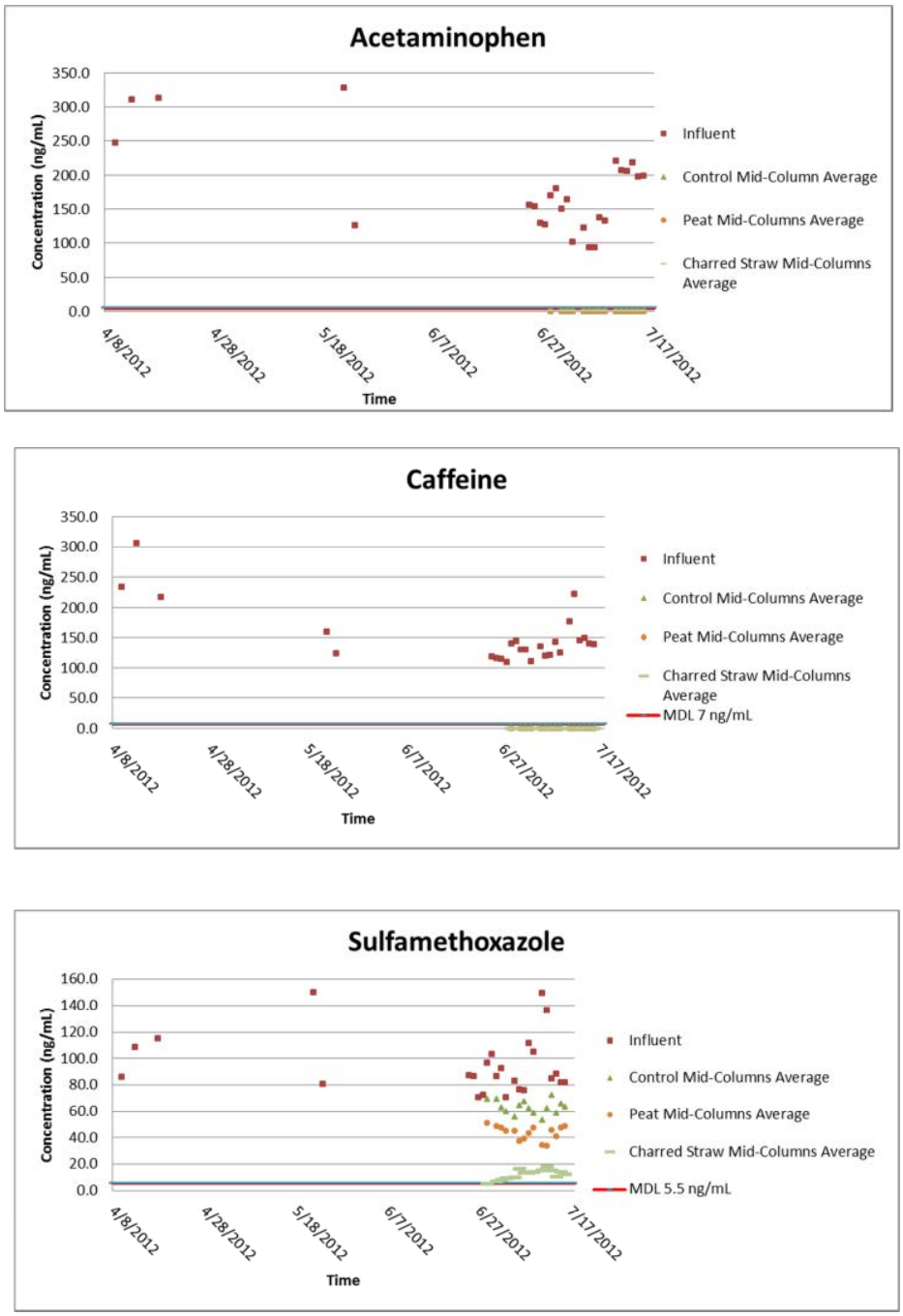


Figure 15: Mid Column Results

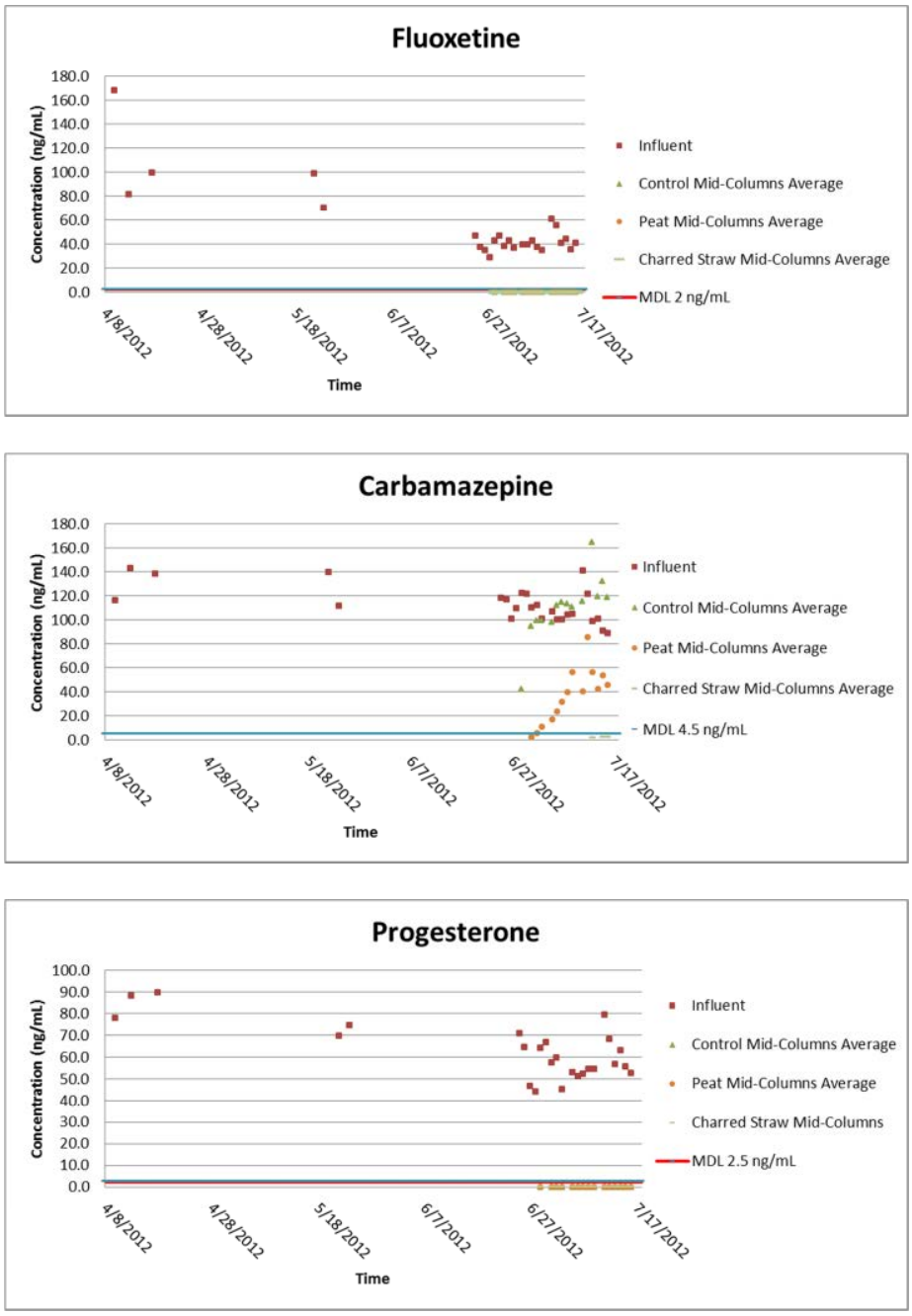


Figure 15 (cont.): Mid Column Results

As was with the case with sulfamethoxazole, carbamazepine reached breakthrough concentration presumably before sampling of the lysimeters began for the

control columns. Exhaustion, or 95% of the initial concentration, was reached in the control columns around the 16th day of pumping. Samples taken from the control columns towards the end of the experiment showed some concentrations of carbamazepine in exceedance of the initial concentrations. This, along with data from the desorption experiment, suggest that desorption may be taking place. One of the peat columns reached carbamazepine breakthrough at day 14 of pumping whereas the other peat column did not reach breakthrough till day 22. Exhaustion was not reached during the experiment's time frame for the peat columns nor was breakthrough or exhaustion reached for the charred straw columns.

As was the case of sampling at the bottom sampling ports, none of the other target PPCPs reached the method detection limit during the time of the experiment nor did the columns reach exhaustion at the lysimeter locations.

Column Study Experiment Discussion

Assuming that sorption is the main mechanism, one can estimate when a compound in a column will occupy its available sorption sites. For example, with a starting concentration 100 ng/mL, soil has a sorptive capacity for carbamazepine of 223 ng/g. This means that 3 feet of soil (25,300 g), the length of soil in each column, would potentially be able to sorb approximately 5.57 mg of carbamazepine. If 888.8 mL (8 liters divided to nine columns) of 100 ng/mL carbamazepine was pumped into the control column each day, it would take potentially 62.7 days for all of the sorption sites to be taken up and reach complete exhaustion. Table 6 shows the estimated time (days) it would take for each of the studied PPCPs to reach complete exhaustion for each column.

Table 6: Estimated Complete Exhaustion

Estimated Complete Exhaustion (days) in the Columns with 888.8 mL/day of 100 ng/mL PPCPs			
	Control Column (Conventional System)	Peat Column (Engineered System)	Charred Straw Column (Engineered System)
Acetaminophen	650.1	662.0	1126.4
Caffeine	246.7	267.3	541.2
Sulfamethoxazole	N/A	32.4*	3.9*
Fluoxetine	3816.7	3879.7	4665.3
Carbamazepine	62.7	101.8	270.2
Progesterone	871.4	898.9	3779.8

***Calculation does not account for sorption in soil since an isotherm was not generated.**

Results from the column study experiment showed that in the amount of time that PPCPs were pumped into the columns, none of the columns reached complete exhaustion. Complete exhaustion was also not attained at the 1 foot interval below the drainfield which, according to the estimation used for Table 6, would have occurred after 21 days of pumping. This may be an indicator that some biodegradation is taking place.

Although neither breakthrough nor exhaustion of the control columns with carbamazepine were reached within the sampling period of the experiment, it is estimated that exhaustion would be reached before the 63rd day of pumping, were the experiment to be continued. Under the same conditions, it is estimated that the peat columns and charred straw columns would reach saturation for carbamazepine at the lysimeters at 25 and 102 days respectively and 90 days and 270 days, respectively, at the base of the column.

With the same assumptions previously mentioned, sulfamethoxazole would be limited mainly on the time required to pass through the column, which if it acts similar to

the bromide tracer, could appear at the base of the columns in as little as six days of pumping. Results showed that concentrations began to appear above the method detection limit around day 9 and 10. Varying explanations could be that bromide is not similar enough to sulfamethoxazole in terms of movement. Also, unsaturated flow conditions could cause varying PPCP flow paths through the soil and cause delays for PPCPs reaching the bottom of the column.

Results from the bromide tracer (Appendix N: Bromide Tracer Results) showed that the concentration of bromide peaked at around 80% of the pore volume, which averaged 4.9 ±0.24 liters of liquid for each column. Figure 16 shows that the bromide tracer is conservative in that it came out of the bottom of the columns much sooner than the target PPCPs. However, this could be due to the concentration of bromide in the tracer being up to 500 times more concentrated than the target compounds, due to analytical constraints.

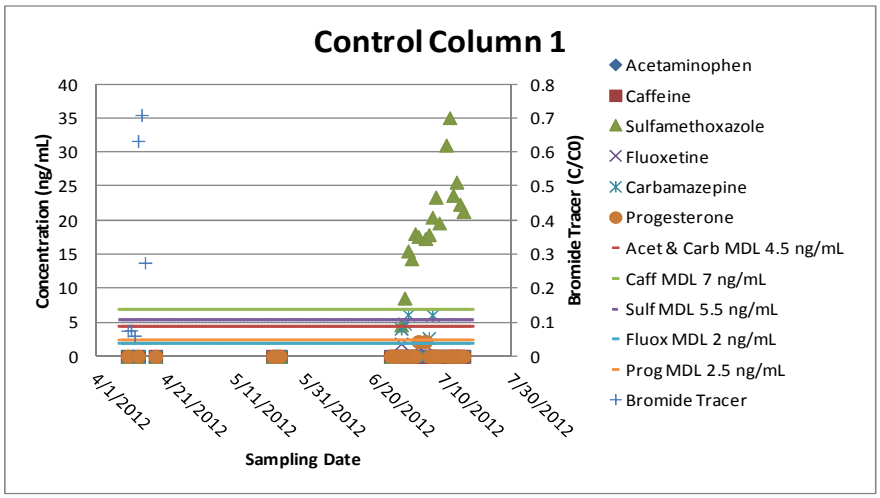


Figure 16: Bottom of Columns with Tracer

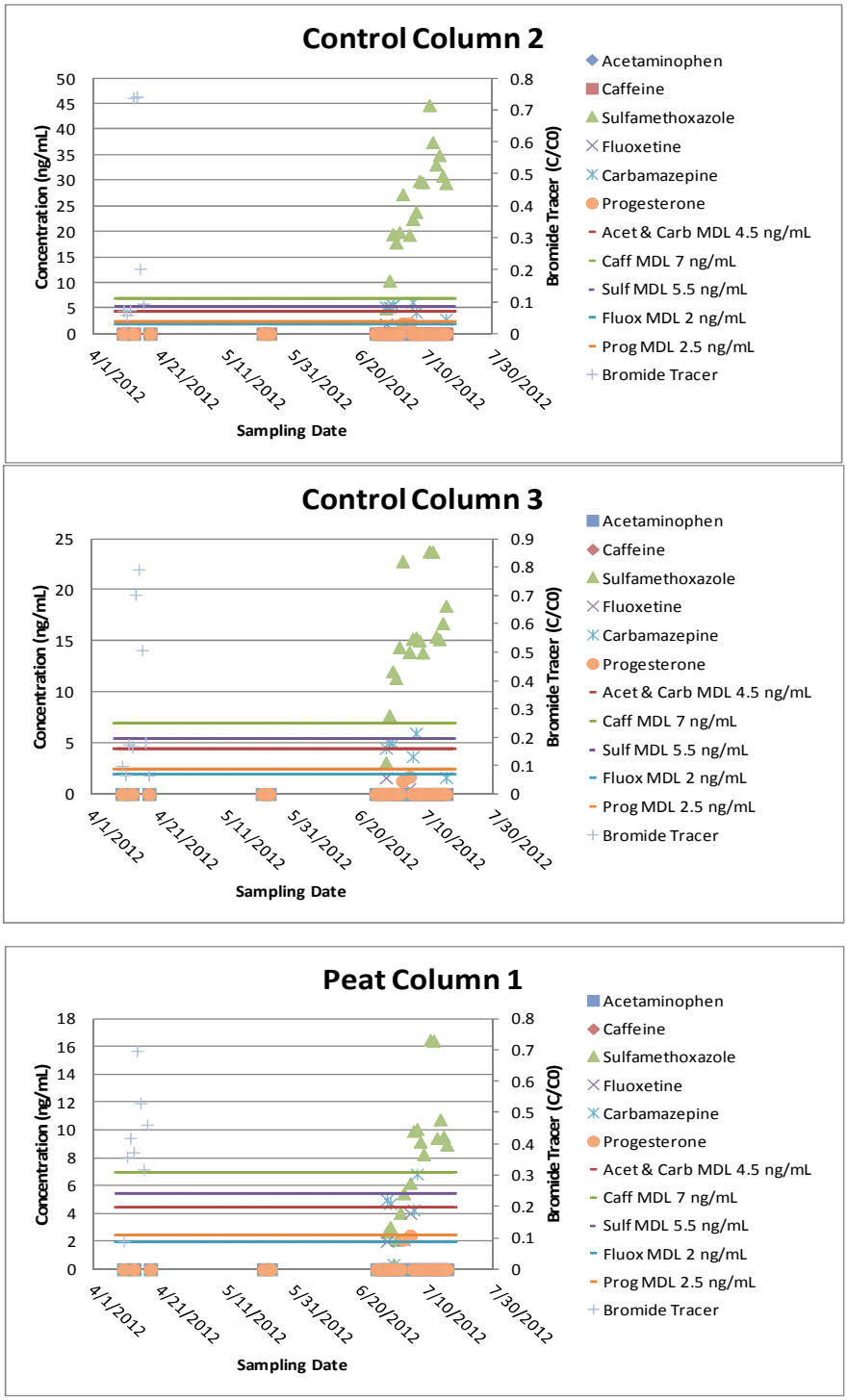
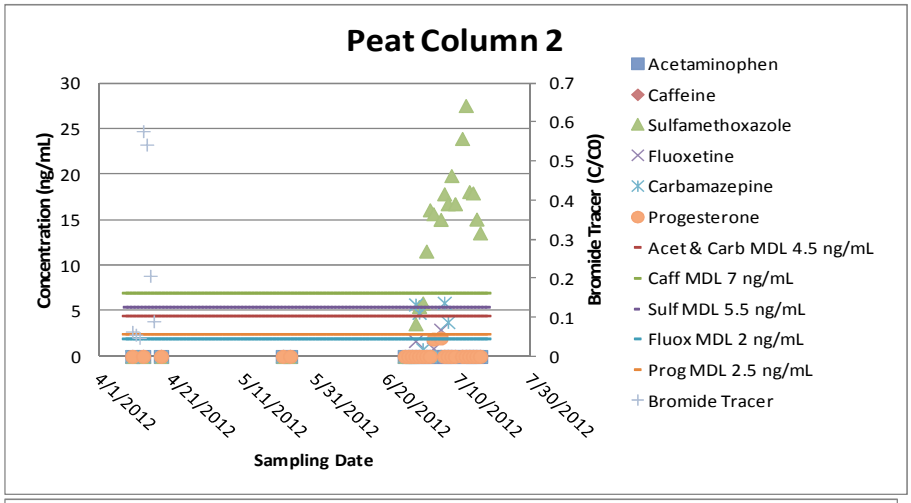
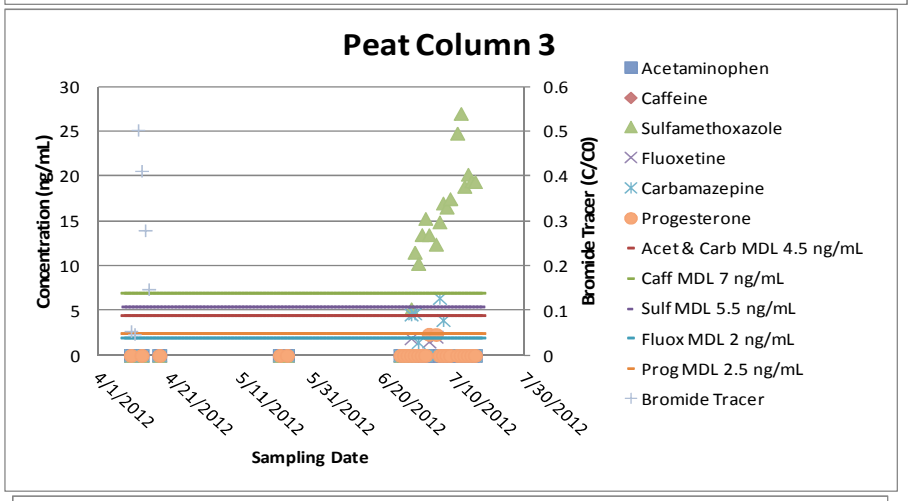


Figure 16 (cont.): Bottom of Columns with Tracer





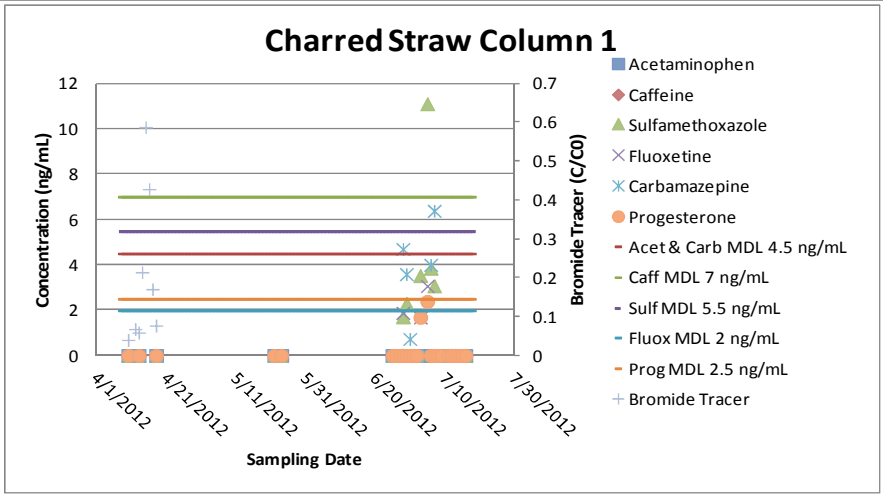


Figure 16 (cont.): Bottom of Columns with Tracer

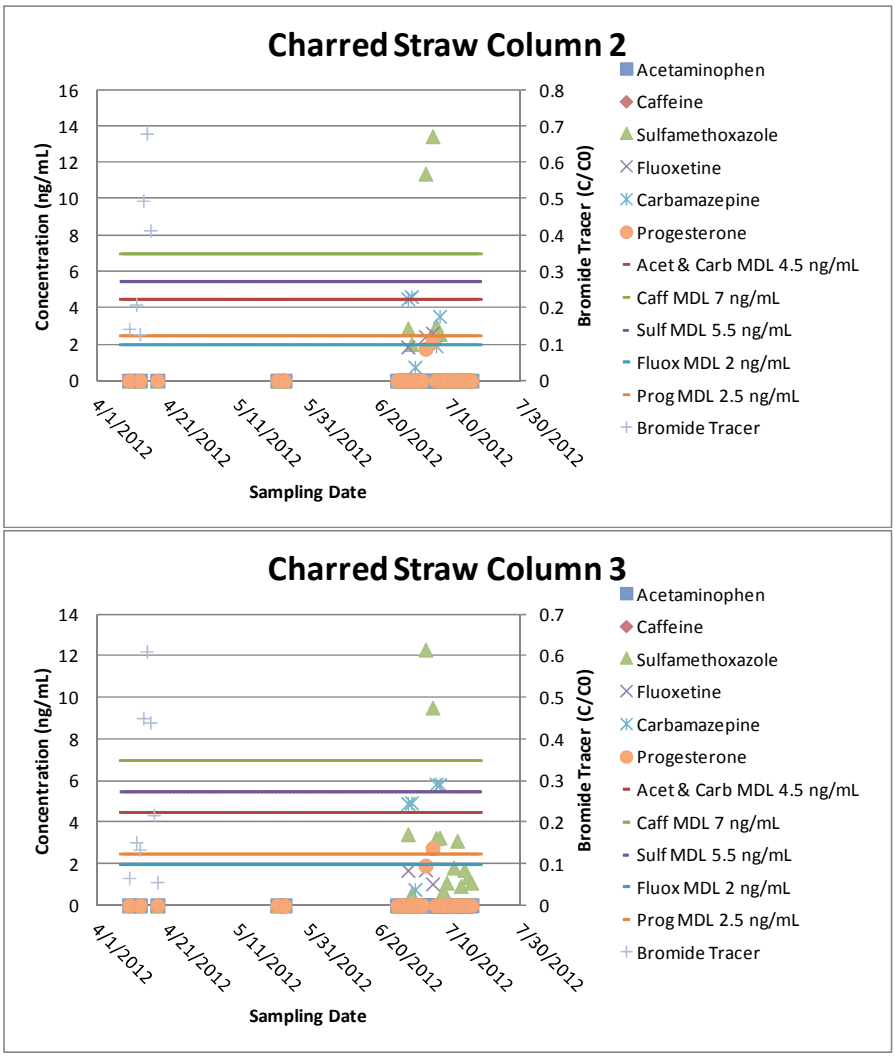


Figure 16 (cont.): Bottom of Columns with Tracer

The explanation that sulfamethoxazole is undergoing some degradation along with sorption is perhaps more likely than it acting as a conservative tracer since results from the column study experiment indicates that sulfamethoxazole concentrations peaked, but were below the initial concentration. Also, even though peat had a greater sorptive capacity for sulfamethoxazole than did charred straw or soil, the charred straw columns had sulfamethoxazole concentrations remaining significantly lower than concentrations in the other columns.

Design Cost

The amount of needed media (peat or charred straw) to add to a drainfield would be based on what PPCPs are being targeted to be removed, and the expected amount (concentration and flow) of PPCPs entering the drainfield; which would be calculated using the isotherms provided earlier.

A conventional (standard trench with pipe and gravel) drainfield, with a percolation rate of 35 minutes per inch, for a three bedroom house, would need around 900 square feet of absorption area. With 3 foot wide trenches, 300 linear feet of drainfield would be needed and would cost approximately $10.00-$15.00 installed (Benjamin Witt, personal communication, April 23, 2013). Using the experiment's design of two inches of media, approximately 177 bales of straw (at roughly 0.85 cubic feet of charred straw per bale) would then be needed which would add an additional cost of $885.00 at $5.00 per bale or an additional $3.00 per linear foot of drainfield.

Using the same trench design but with peat as the added media would require approximately 150 cubic feet of peat which would cost around $600.00 at $4.00 per cubic foot of peat or an additional $2.00 per linear foot of drainfield. Therefore the installation of a conventional drainfield with charred straw added would cost approximately $13.00 to $18.00 per linear foot of drainfield whereas a conventional drainfield with peat added would cost approximately $12.00 to $17.00 per linear foot of drainfield.

CHAPTER VII

CONCLUSION

Isotherm Study

Sorption isotherms are used to approximate the quantity of sorbate that can be taken up by an sorbent. Based on comparison of the sorption isotherm and residual calculations, the linear Freundlich isotherm was chosen as the best equation to describe the experimental isotherm data. Linear Freundlich isotherms were generated for most of the media and their target compounds with the exception of soil with sulfamethoxazole (too low to quantify), charred straw with acetaminophen, caffeine, fluoxetine, carbamazepine, and progesterone; and peat with progesterone (poor correlation coefficients).

The linear Freundlich isotherms were used to estimate the sorptive capacity of the different media (Table 4) with the target PPCPs. Overall, peat had the greatest sorptive capacities of the media used.

Sorption and Biodegradation Experiment

Batch reactors were used to investigate whether the main PPCP reducing mechanism was sorption, biodegradation, or volatilization/hydrolysis. Degradation (sorption/biodegradation) was assumed to be a 1^{st} order reaction and therefore reaction constants were attained by graphing log transforms. PPCP reduction due to volatilization/hydrolysis was minimal. It was assessed that the main mechanism for PPCP removal is sorption, with the exception of progesterone in which degradation plays

a significant role. Caffeine had the largest sorption/degradation constant with soil versus the media. Desorption results indicated that caffeine can desorb from soil.

Column Study Experiment

As hypothesized, the lowest percent removed PPCP were sulfamethoxazole and carbamazepine. The other PPCPs were not detected during the time period the experiment was conducted and therefore it is difficult to further conclude which of the compounds would continue to have the largest total percent removal. It can, however, be hypothesized that based upon the degradation constants estimated in the sorption and degradation experiment, and because of its polar property, fluoxetine would most likely continue the longest as having complete removal in a both conventional and engineered septic system drainfields.

The column study showed that overall, conventional and engineered on-site wastewater drain fields are effective at reducing PPCP concentrations from potentially leaving the drain field and entering the water table. Both the peat and especially the charred straw engineered drain fields outperformed the control drainfield in that they were able to remove, if not retard, even the more mobile target compounds such as carbamazepine and sulfamethoxazole.

Engineering Significance

With improved analytical methods and the growing dependence upon PPCPs, concern over the fate of PPCPs in the environment has likewise grown. It is important to know what happens to the PPCPs that we take into our bodies and then eliminate into the environment and how the environment, in turn, responds to the PPCPs. If engineered

controls, such as a septic system drainfield (conventional or engineered), can possibly reduce or eliminate introduction of these PPCPs to the environment, then concern over their fate can be lessened. This also would decrease the chance of over exposure to humans, such as in drinking water sources, and to wildlife. Understanding the fate of PPCPs can also help in choosing treatment technologies for wastewater such as whether a centralized treatment plant or an on-site wastewater treatment system may be more effective for removal of PPCPs.

This study has shown that on-site wastewater treatment systems have potential for removing or reducing PPCPs, such as caffeine, acetaminophen, progesterone, and fluoxetine and that treatment is due primarily to sorption. On-site wastewater treatment systems engineered by using peat or charred straw at the bottom of the drainfield were more effective at removing these PPCPs than conventional drain fields. Out of the two media used in the engineered drain fields, charred straw had the greater PPCP removal. This information could be used to change the way drain fields are designed. Isotherm data from this study could be used to design future septic system drain fields by calculating the amount of sorbent needed based on expected PPCP concentrations, to increase PPCP removal efficiencies. Using drain fields engineered with charred straw could make on-site systems an effective wastewater treatment practices that is also effective at PPCP removal.

Future Recommendations

Recommendations for future similar experiments would be to investigate the fate of these target compounds, along with additional PPCPs, for longer periods of time, maybe in terms of years and to investigate whether microorganisms in the drainfield gain

a resistance to the compounds or adapt to become more efficient at degrading them. It would be interesting to see the effect concentration would have on the system, i.e., if the concentrations were more similar to that of the tracer, they would behave more closely to the tracer. In addition to investigating the fate of the target compounds, it would be helpful to know the fate of the target compound's metabolites, which could better explain how much of the target compounds were degraded versus being sorbed. A field study using both new and mature drainfields could be helpful in determining the effects drainfield microorganisms have at PPCP reduction, as would different styles of drainfields such as standard versus deep trench. It is also recommended to investigate if the lifespan of the drainfield changes with modifications such as adding charred straw or peat and if/how the modifications might change biomat formation. A more extensive study investigating the effects the engineered drain fields have on removing nutrients and BOD_5 would also be encouraged.

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APPENDICES

A Absorption Trench Construction Details

TABLE 8

Absorption Trench Construction Details(a)

ITEM	UNIT	MINIMUM	MAXIMUM
GRAVITY EFFLUENT DISTRIBUTION PIPES:			
Number of laterals	--	2(b)	--
Length of individual laterals	feet	--	100(c)
Diameter	inches	4	--
Width of trenches	inches	12	36
Slope of distribution pipe	inches/100 ft. (d)	4	
Depth to trench bottom (from ground surface)	inches	10	(e)
Distance between trenches	(see R317-4-9, Table 9)		
Bottom of trench to maximum ground water table	inches	24	--
Bottom of trench to unsuitable soil or bedrock formations	inches	48	--
SIZE OF FILTER MATERIAL	inches	3/4	2-1/2
Allowable fines:			
1/2 inch mesh(a) (12.5 millimeter)	percent	0	5
#10 mesh(a) (2.0 millimeter)	percent	0	2

(a) US Standard Sieves

DEPTH OF FILTER

MATERIAL:			
Under distribution pipe	inches	6(f)	--
Over distribution pipe	inches	2	--
Total depth	inches	12	--
Under pipe located within 10 feet of trees and shrubs	inches	12	--
THICKNESS OF COMPACTED STRAW BARRIER OVER AGGREGATE FILTER MATERIAL	inches	2	--
DEPTH OF BACKFILL OVER BARRIER COVERING FILTER MATERIAL	inches	6(g)	--

FOOTNOTES

(a) The effective absorption area shall be considered as the total bottom area of the trenches in square feet.

(b) Of near equal length.

(c) Preferably not more than 60 feet long.

(d) Preferably level.

(e) Trenches should be constructed as shallow as is practical to allow for evapotranspiration of wastewater.

(f) Preferably 8 inches.

(g) Whenever any distribution pipes will be covered with between six and 12 inches of backfill, they shall be laid level, and adequate precautions shall be made to prohibit traffic or heavy equipment from the disposal area.

(The Department of Administrative Rules 2011)

B Soil Properties

Soil Test Report

and

Fertilizer Recommendations

USU Analytical Labs
Utah State University
Logan, Utah 84322-4830
(435) 797-2217
(435) 797-2117 (FAX)
www.usual.usu.edu

Date Received: 11/29/2011
Date 12/1/2011
Name: JAMES BEARDALL
Address: 335 S MAINT ST BSMT

PROVIDENCE UT 84332

Phone: 801 913 6720
County: CACHE

Lab Number: 1101-2309
Identification: DM 8
Crop to be Grown:

Grower's Comments:

Acres in Field:

Soil Test		Interpretations	Recommendations
Texture	Sandy Loam		
pH	8.3	Normal	
Salinity - ECe	0.2		
Phosphorus - P	3.2		
Potassium - K	72.0		
Nitrate-Nitrogen - N mg/kg	1.59		
Zinc - Zn	0.64		
Iron - Fe mg/kg	1.37	Very Low	
Copper - Cu	0.31	Adequate	
Manganese - Mn	1.89	Adequate	
Sulfate-Sulfur - S	0.4	Low	
Organic Matter	0.7		
SAR			

Note

FOR INTERPRETATIONS / RECOMMENDATIONS, PLEASE CONTACT THE LAB WITH INFORMATION ON WHAT YOU WILL BE GROWING (NOT INDICATED ON INFORMATION SHEET RECEIVED).

For further assistance, please see your County Agent

For further information and publications of interest, see

USU Analytical Lab webpage or Utah State University Extension

Soil Test Report

and

Fertilizer Recommendations

USU Analytical Labs
Utah State University
Logan, Utah 84322-4830
(435) 797-2217
(435) 797-2117 (FAX)
www.usual.usu.edu

Date Received: 11/29/2011
Date 12/1/2011
Name: JAMES BEARDALL
Address: 335 S MAINT ST BSMT

PROVIDENCE UT 84332

Phone: 801 913 6720
County: CACHE

Lab Number: 1101-2310
Identification: DM 16
Crop to be Grown:

Grower's Comments:

Acres in Field:

Soil Test		Interpretations	Recommendations
Texture	Sandy Loam		
pH	8.2	Normal	
Salinity - ECe	0.2		
Phosphorus - P	2.0		
Potassium - K	71.6		
Nitrate-Nitrogen - N mg/kg	1.61		
Zinc - Zn	0.32		
Iron - Fe mg/kg	1.39	Very Low	
Copper - Cu	0.82	Adequate	
Manganese - Mn	3.08	Adequate	
Sulfate-Sulfur - S	0.3	Low	
Organic Matter	0.7		
SAR			

Note

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For further information and publications of interest, see

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Soil Test Report

and

Fertilizer Recommendations

USU Analytical Labs
Utah State University
Logan, Utah 84322-4830
(435) 797-2217
(435) 797-2117 (FAX)
www.usual.usu.edu

Date Received: 11/29/2011
Date 12/1/2011
Name: JAMES BEARDALL
Address: 335 S MAINT ST BSMT

PROVIDENCE UT 84332

Phone: 801 913 6720
County: CACHE

Lab Number: 1101-2311
Identification: DM 24
Crop to be Grown:

Grower's Comments:

Acres in Field:

Soil Test		Interpretations	Recommendations
Texture	Loamy Sand		
pH	8.0	Normal	
Salinity - ECe	0.4		
Phosphorus - P	2.3		
Potassium - K	59.9		
Nitrate-Nitrogen - N mg/kg	5.41		
Zinc - Zn	0.06		
Iron - Fe mg/kg	1.58	Very Low	
Copper - Cu	0.14	Low	
Manganese - Mn	3.55	Adequate	
Sulfate-Sulfur - S	1.3	Low	
Organic Matter	0.5		
SAR			

Note

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For further assistance, please see your County Agent

For further information and publications of interest, see

USU Analytical Lab webpage or Utah State University Extension

12/21/2011

James Beardall
335 South Main St. Bsmt
Providence, UT 84332

Samples Received: 12/13/11

USU ID	Identification	Cation Exchange Capacity cmol/kg
7031	Soil	7.2
7032	Peat	30.1
7033	Charred Straw	6.5

C EPI - Chemical Properties

		Calculated using EPI-Suite (US EPA 2011)							
Name	**Molecule**	**MW**	**MP (°C)**	**BP (°C)**	**Pv (atm)**	**S (mg/L)**	**logKow**	**log Koc**	**log Kaw**
Caffeine	C8H10N4O2	194.19	238	430.85	9.64E-12	21600	-0.07	1	-8.83
Acetaminophen	C8 H9 N1 O2	151.17	170	340.65	1.94E-06	14000	0.46	1.65	-10.58
Carbamazepine	C15 H12 N2 O1	236.28	190	410	1.16E-10	112	2.45	3.12	-8.36
Sulfamethoxazole	C10 H11 N3 O3 S1	253.28	167	414.01	1.71E-10	610	0.89	2.41	-10.4
Progesterone	C21 H30 O2	314.47	121	396	3.54E-09	8.81	3.87	4	-5.57
Fluoxetine	C17 H18 F3 N1 O1	309.33	105	347	3.32E-08	61.28	4.05	4.97	-5.43

	Calculated using log Koc, S, Pv from EPI-Suite					
Name	**Kd**	**log Kd**	**Ksw**	**log Ksw**	**Kaw**	**log Kaw**
Caffeine	0.2	-6.99E-01	5.00E-01	-0.3	3.55E-12	-1.14E+01
Acetaminophen	0.9	-4.50E-02	2.25E+00	0.35	8.57E-07	-6.07E+00
Carbamazepine	26.5	1.42E+00	6.64E+01	1.82	1.00E-08	-8.00E+00
Sulfamethoxazole	5.16	7.13E-01	1.29E+01	1.11	2.91E-09	-8.54E+00
Progesterone	201	2.30E+00	5.03E+02	2.7	5.17E-06	-5.29E+00
Fluoxetine	1870	3.27E+00	4.68E+03	3.67	6.85E-06	-5.16E+00

D EPI - Suite STP Removal and Level III Fugacity

(US EPA 2011)

Caffeine

Removal in Wastewater Treatment:

Total removal: 75.07%
Total biodegradation: 74.45%
Total sludge adsorption: 0.62%
Total to Air: 0.00%

Level III Fugacity Model:

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	2.75E-7	13.2	0
Water	39.2	360	5.34E-8
Soil	60.7	720	5.34E-8

Persistence Time: 578 hrs.

Acetaminophen

Removal In Wastewater Treatment:

Total removal: 75.09%
Total biodegradation: 74.46%
Total sludge adsorption: 0.63%
Total to Air: 0.00%

Level III Fugacity Model:

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	9.1E-12	14.5	0
Water	31.1	360	5.34E-8
Soil	68.8	720	5.34E-8

Persistence Time: 636 hrs.

Carbamazepine

Removal In Wastewater Treatment:

Total removal:	24.51%
Total biodegradation:	22.09%
Total sludge adsorption:	2.42%
Total to Air:	0.00%

Level III Fugacity Model:

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	1.79E-8	0.813	0
Water	18.1	900	5.34E-8
Soil	80.5	1800	5.34E-8

Persistence Time: 1580 hrs.

Sulfamethoxazole

Removal In Wastewater Treatment:

Total removal:	22.05%
Total biodegradation:	20.57%
Total sludge adsorption:	1.47%
Total to Air:	0.00%

Level III Fugacity Model:

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	5.88E-12	1.28	0
Water	20.6	900	5.34E-8
Soil	79.1	1800	5.34E-8

Persistence Time: 1.49e+003 hrs.

Progesterone

Removal In Wastewater Treatment:

Total removal:	40.20%
Total biodegradation:	18.18%
Total sludge adsorption:	22.01%

Total to Air: 0.00%

Level III Fugacity Model:

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	4.82E-5	2.24	0
Water	12.4	1440	5.34E-8
Soil	78.2	2880	5.34E-8

Persistence Time: 2.64e+003 hrs.

Fluoxetine

Removal In Wastewater Treatment:

Total removal: 37.79%
Total biodegradation: 17.41%
Total sludge adsorption: 20.37%
Total to Air: 0.00%

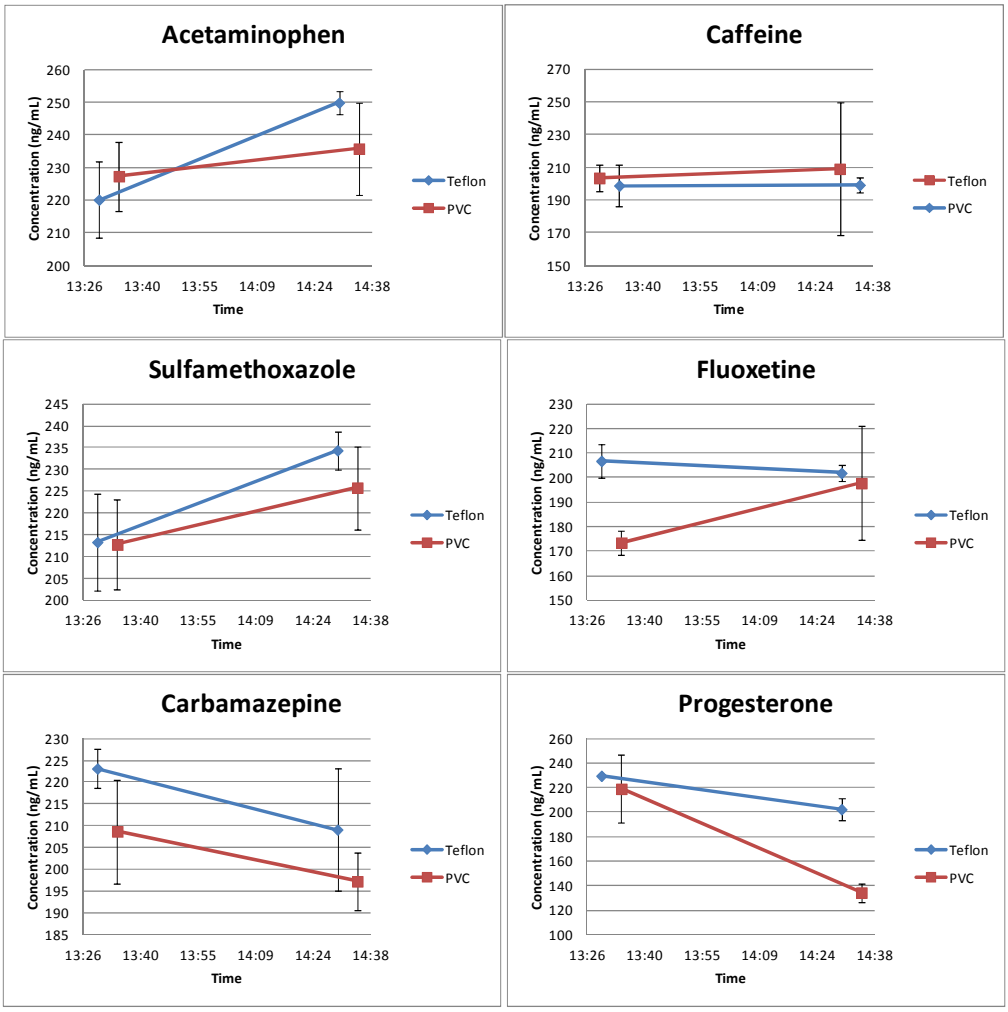
Level III Fugacity Model:

	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	4.2E-5	6.96	0
Water	6.37	1440	5.34E-8
Soil	51.9	13000	5.34E-8

Persistence Time: 4e+003 hrs.

E Tube Test

All samples were measured in triplicate and averaged. Error bars indicate the 95% confidence interval. Initial concentrations were 200 ng/mL.



F Homeowner Survey

RESIDENTIAL EVALUATION SURVEY

Address: [redacted]

Name of Homeowner(s): [redacted]

Home/Residents

1. Is this your first home with an on-site wastewater treatment system? (YES) / NO
2. Did you receive any septic system user information when you moved into the home? YES / (NO)
3. Did you receive the as-built drawing (shows actual layout) for the system? YES / (NO)
4. Type of use: (Permanent) / Seasonal If seasonal, number of months used _____
   a. Number of people living in the home: Adults: 1 M 1 F
   b. Children: ___ M ___ F Teenagers: 1 M ___ F
   c. Number of bedrooms: 4 Number of bathrooms: 2
5. Water supply: (Private well) / Centralized system / Other supply
   a. If you have a private well how close is the well located to the drainfield (circle below)?
      Less than 50 ft 50 – 99 ft (100 – 150 ft) Greater than 150 ft
6. Do you have an in-home business? YES / (NO)
   If "yes", what type? _____
7. Does any resident use long term prescription drugs or antibiotics? (YES) / NO
   Type Wellbutrin, HRT, Omezparole, High Cholesterol, High Blood Pressure Meds.
8. Do you use bath/skin oil/moisturizer? Lotion (YES) NO
   Use: 7 times/week.
9. Do you use septic system additives? YES / (NO)
   If "yes", what products? _____

Appliances and Cleaning Products

10. Home equipped with water conserving fixtures/appliances? YES / (NO)
11. Garbage disposal? YES / (NO) Use: _____ times/day _____ times/week
12. Dishwasher used? (YES) / NO Use: 1 times/day 7 times/week
13. Laundry: Maximum _____ loads per day Consecutive loads: YES / (NO)
    Total 5 loads/week
    a. Brand of laundry detergents used? Melaleuca powder / (liquid)
    b. Bleach used? YES / (NO) powder / liquid Use: _____ cups/load _____ loads/week
14. Whirlpool tub? YES / (NO) Use: _____ times/day _____ times/week
15. Is a drain cleaner used? (YES) / NO Type: Generic
    Frequency of use: 1 every 6 wks
16. Hand-washing soap brand? Generic Antibacterial? YES / (NO)
17. Number of rolls of toilet paper used per week? 3-4 (don't really know)

18. Toilet cleaning product brand? Generic Cleanings/month 2
Continuous cleaner used in toilet tank? YES / (NO)

19. Please list commonly used cleaning supplies:
Shower Soft Scrub Kitchen Bar keepers
Floors Pine Sol Other: _____

20. Please list any antibacterial products: ~

21. Water treatment device: (YES) / NO
a. Is a water softener used? (YES) / NO Backflushes to: not sure - septic tank?
b. Reverse osmosis? (YES) / NO Discharges to: septic tank?
c. Other: _____

22. Air conditioner unit(s)? (YES) / NO condensate drains to: ?

23. Swamp Cooler(s)? YES / (NO) condensate drains to: _____

24. Footing drains or basement sump pumps connected into the system? (YES) / NO

System

25. Do you have a septic tank connected to your system: (YES) / NO
Septic Tank Size: no idea gallons

26. How old is the septic system? 11 years Date of last pump out: 8/2005

27. Has the system ever backed up? YES / (NO)

28. Have the baffles ever been plugged? YES / (NO)

29. Effluent filter in septic tank outlet? YES / NO ?

30. Has effluent filter ever plugged? YES / NO Date(s): ?

31. Has the system ever been repaired? YES / (NO)

32. Has effluent ever surfaced? YES / (NO)

33. Has the alarm ever sounded? YES / (NO) / NA

34. Soil type – at drainfield depth or lower: Clay

35. Type of distribution/dispersal system: ☑Shallow Trench ? ☐Deep Wall Trench ☐ Pressure dose
☐Seepage pit ☐Absorption bed ☐Other: _____

36. If answered "pressure dose" on Question 35,
Control system: Demand / Timed

Fertilizer and Animal Waste

37. Do you have either a yard or garden? (ONLY CIRCLE ONE) (YES) NO
If No, skip to question #39, otherwise please continue.

38. Which of the following best describes the use of fertilizers, pesticides, or herbicides on your yard or garden? (ONLY CIRCLE ONE)
(a.) You yourself apply these
b. An outside service applies these
c. No one applies these

39. How are fertilizers, pesticides, or herbicides usually disposed of when you have some leftover? (ONLY CIRCLE ONE)
a. Put it in the street
(b.) Store it and use it later
c. Take it to a recycling center
d. Put it in the trash
e. Pour it down the drain
f. Other (please specify): _____

40. About how often are fertilizers (just fertilizers) applied on your yard or garden?
a. More than once / week
b. Once/week
c. Once/month
d. A few times each year
e. Once/year
(f.) Never

41. Do you own outdoor animals of any kind? (YES) NO
If yes, what kind and how many?
a. Cats #: 1
b. Dogs #: 1
c. Horses #: 2
d. Pigs #: _____
e. Cows #: _____
f. Sheep #: _____
g. Other (please specify kind & #): _____

42. How are animal waste products handled?
a. Collected into manure piles and used as fertilizer on your own property
b. Collected into manure piles and used as fertilizer on someone else's property
(c.) Put in trash can
d. Disposed of in pit on property
e. Nothing (left where it lands)
f. Other (please specify): _____

Water Use

43. How do you feel that the quality of your drinking water has changed over the last 10 years?
a. It has gotten better.
b. It has gotten worse.
c. It has not changed.
(d.) I haven't lived in Castle Valley for 10 years.

44. If current trends and conditions continue over the next 10 years, how do you feel the quality of your drinking water will change?
a. It will get better.
b. It will get worse.
(c.) It will stay the same.

45. Do you have actual water use information (Gal / day)?
Average: _____ High: _____ Low: _____
How is water use measured? _____

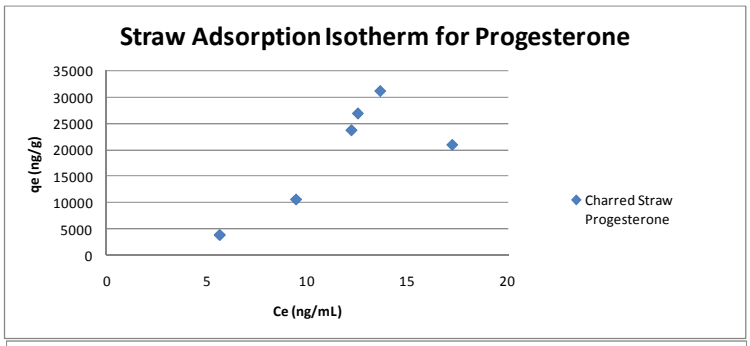
G Isotherm Results

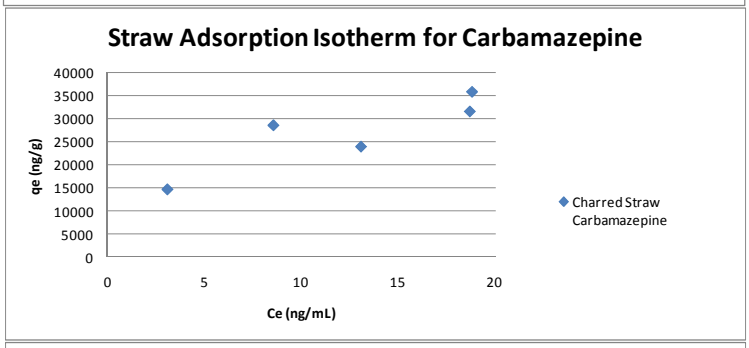
Sorbent	Sorbent mass (g)	Sorbate	Initial Concentration (ng/mL)	Final Concentration (ng/mL)
Soil	7.5	Acetaminophen	487.64	18.64
Soil	7.5	Acetaminophen	696.18	82.83
Soil	7.5	Acetaminophen	779.75	76.41
Soil	7.5	Acetaminophen	909.25	147.49
Soil	7.5	Caffeine	48.91	8.11
Soil	7.5	Caffeine	94.95	14.40
Soil	7.5	Caffeine	200.25	40.72
Soil	7.5	Caffeine	503.99	120.12
Soil	7.5	Caffeine	581.40	187.46
Soil	7.5	Caffeine	676.80	240.25
Soil	7.5	Caffeine	765.50	302.62
Soil	7.5	Sulfamethoxazole	12.48	13.41
Soil	7.5	Sulfamethoxazole	20.02	18.82
Soil	7.5	Sulfamethoxazole	51.24	67.54
Soil	7.5	Sulfamethoxazole	107.65	123.84
Soil	7.5	Sulfamethoxazole	240.73	267.15
Soil	7.5	Sulfamethoxazole	482.88	630.42
Soil	7.5	Sulfamethoxazole	686.39	781.55
Soil	7.5	Sulfamethoxazole	755.42	955.96
Soil	7.5	Sulfamethoxazole	888.72	1133.62
Soil	7.5	Fluoxetine	474.60	1.98
Soil	7.5	Fluoxetine	704.94	4.20
Soil	7.5	Fluoxetine	784.78	5.07
Soil	7.5	Fluoxetine	923.70	6.49
Soil	7.5	Carbamazepine	13.00	5.26
Soil	7.5	Carbamazepine	20.73	8.55
Soil	7.5	Carbamazepine	52.85	28.38
Soil	7.5	Carbamazepine	111.52	56.11
Soil	7.5	Carbamazepine	237.43	127.59
Soil	7.5	Carbamazepine	461.18	302.38
Soil	7.5	Carbamazepine	675.61	475.83
Soil	7.5	Carbamazepine	764.09	563.80
Soil	7.5	Carbamazepine	860.10	673.53
Soil	7.5	Progesterone	95.55	2.28
Soil	7.5	Progesterone	206.76	9.66
Soil	7.5	Progesterone	448.28	24.71

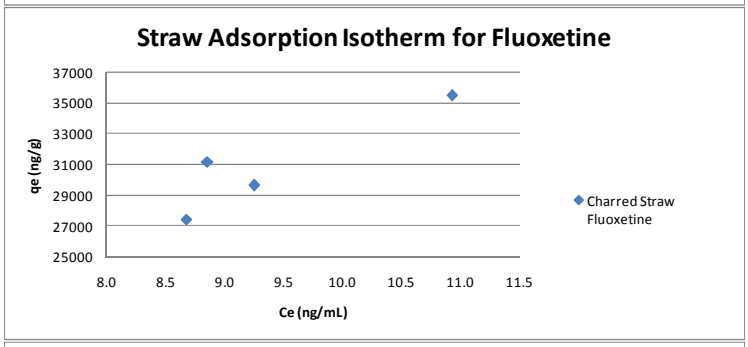
Sorbent	Sorbent mass (g)	Sorbate	Initial Concentration (ng/mL)	Final Concentration (ng/mL)
Soil	7.5	Progesterone	643.30	46.61
Soil	7.5	Progesterone	721.42	62.33
Peat	0.85	Acetaminophen	17.70	6.43
Peat	0.85	Acetaminophen	52.15	23.47
Peat	0.85	Acetaminophen	98.35	42.49
Peat	0.85	Acetaminophen	203.96	86.77
Peat	0.85	Acetaminophen	635.64	275.61
Peat	0.85	Caffeine	51.71	18.77
Peat	0.85	Caffeine	89.16	28.20
Peat	0.85	Caffeine	197.48	50.94
Peat	0.85	Caffeine	518.60	181.81
Peat	0.85	Caffeine	557.31	153.81
Peat	0.85	Sulfamethoxazole	52.00	8.60
Peat	0.85	Sulfamethoxazole	101.46	14.96
Peat	0.85	Sulfamethoxazole	192.74	34.59
Peat	0.85	Sulfamethoxazole	623.56	113.92
Peat	0.85	Sulfamethoxazole	619.36	177.50
Peat	0.85	Fluoxetine	47.90	3.60
Peat	0.85	Fluoxetine	108.63	6.98
Peat	0.85	Fluoxetine	195.60	14.41
Peat	0.85	Fluoxetine	609.83	79.66
Peat	0.85	Carbamazepine	54.32	4.87
Peat	0.85	Carbamazepine	105.98	13.73
Peat	0.85	Carbamazepine	198.34	29.61
Peat	0.85	Carbamazepine	587.78	94.58
Peat	0.85	Carbamazepine	651.62	144.01
Peat	0.85	Progesterone	92.25	4.50
Peat	0.85	Progesterone	159.51	42.82
Peat	0.85	Progesterone	573.90	165.89
Peat	0.85	Progesterone	543.32	12.39
Straw	1.1	Acetaminophen	782.24	14.87
Straw	0.55	Acetaminophen	616.75	20.94
Straw	0.55	Acetaminophen	722.56	27.03
Straw	0.55	Acetaminophen	808.31	24.58
Straw	1.1	Caffeine	924.25	9.64
Straw	0.55	Caffeine	548.20	7.76
Straw	0.55	Caffeine	632.69	12.07
Straw	0.55	Caffeine	733.64	11.22
Straw	1.1	Sulfamethoxazole	12.24	10.66
Straw	1.1	Sulfamethoxazole	26.26	18.73

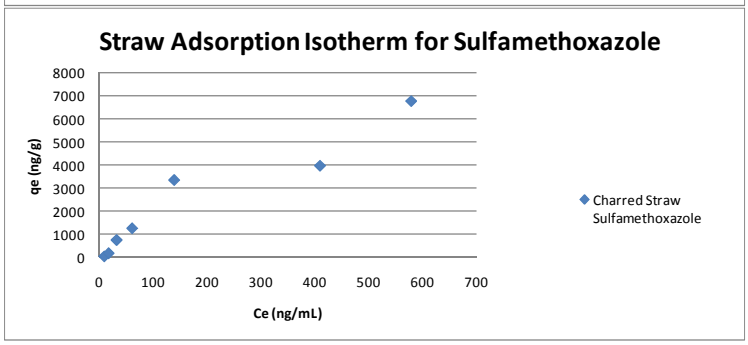
Sorbent	Sorbent mass (g)	Sorbate	Initial Concentration (ng/mL)	Final Concentration (ng/mL)
Straw	1.1	Sulfamethoxazole	117.44	62.23
Straw	1.1	Sulfamethoxazole	287.41	139.86
Straw	1.1	Sulfamethoxazole	584.71	409.64
Straw	1.1	Sulfamethoxazole	877.01	578.24
Straw	0.55	Sulfamethoxazole	594.76	551.55
Straw	0.55	Sulfamethoxazole	681.15	660.33
Straw	0.55	Sulfamethoxazole	777.19	774.13
Straw	1.1	Fluoxetine	1314.20	9.25
Straw	0.55	Fluoxetine	612.30	8.67
Straw	0.55	Fluoxetine	694.38	8.86
Straw	0.55	Fluoxetine	791.81	10.92
Straw	1.1	Carbamazepine	648.37	3.11
Straw	1.1	Carbamazepine	1066.90	13.08
Straw	0.55	Carbamazepine	637.35	8.57
Straw	0.55	Carbamazepine	713.56	18.69
Straw	0.55	Carbamazepine	808.07	18.80
Straw	1.1	Progesterone	175.02	5.62
Straw	1.1	Progesterone	475.53	9.43
Straw	1.1	Progesterone	939.84	17.23
Straw	0.55	Progesterone	534.35	12.19
Straw	0.55	Progesterone	604.70	12.52
Straw	0.55	Progesterone	699.56	13.64

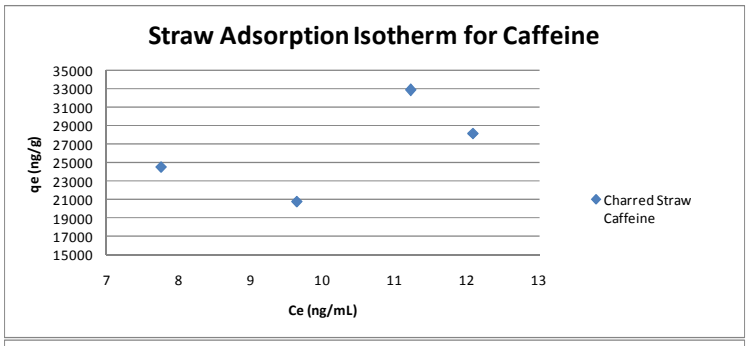
H Sorption Isotherms

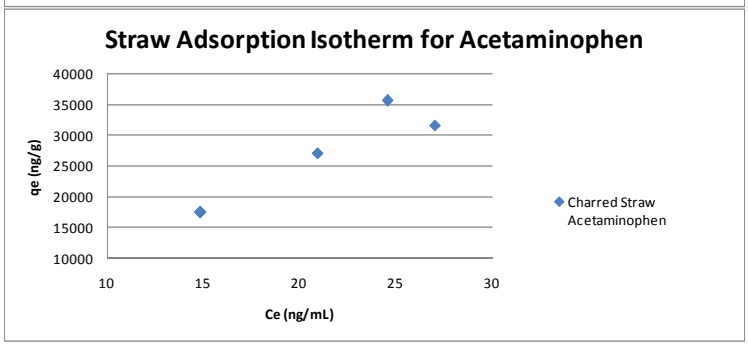


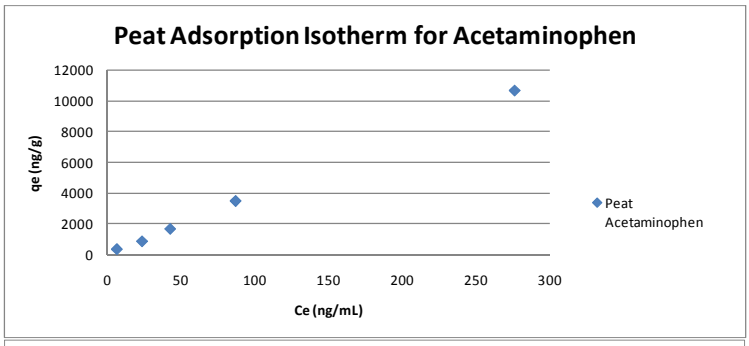


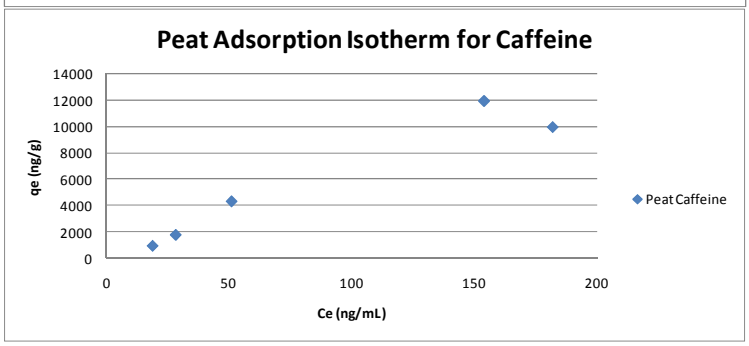


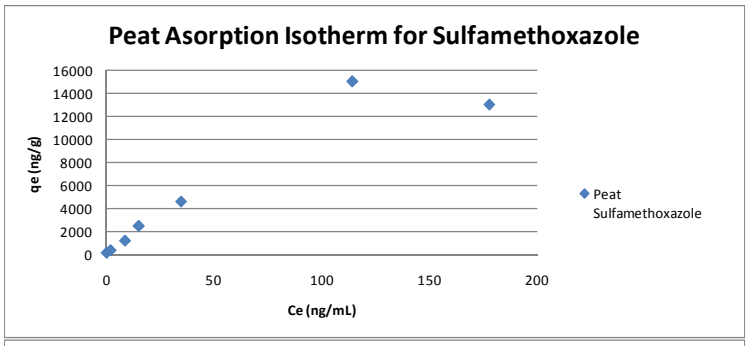


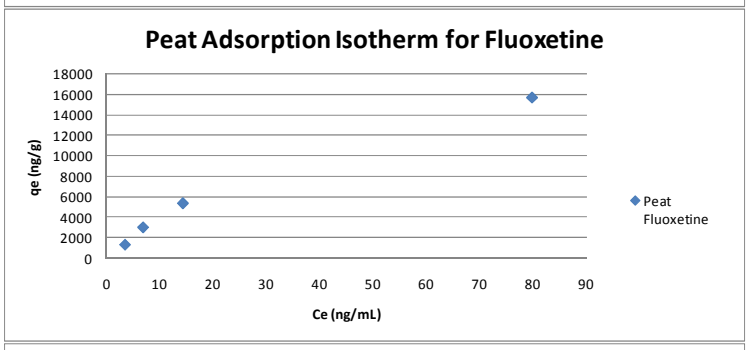

Straw Adsorption Isotherm for Caffeine
qe (ng/g)
35000
33000
31000
29000
27000
25000
23000
21000
19000
17000
15000
7
8
9
10
11
12
13
Ce (ng/mL)
Charred Straw Caffeine

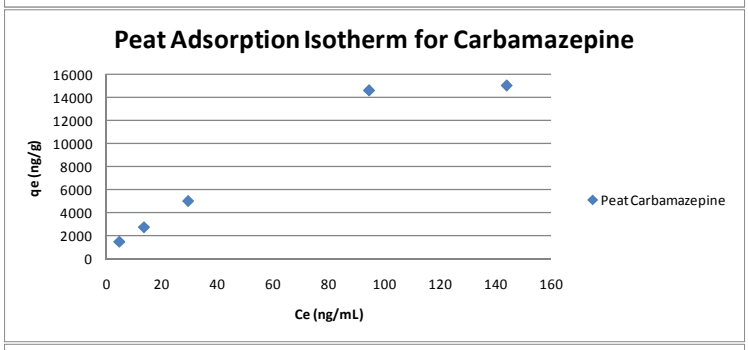

Straw Adsorption Isotherm for Acetaminophen
qe (ng/g)
40000
35000
30000
25000
20000
15000
10000
10
15
20
25
30
Ce (ng/mL)
Charred Straw Acetaminophen

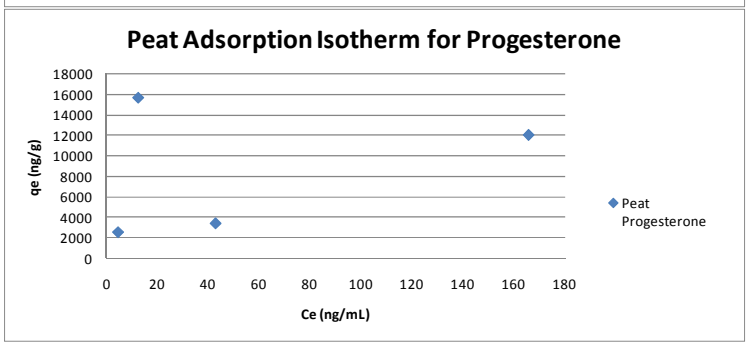

Peat Adsorption Isotherm for Acetaminophen
qe (ng/g)
12000
10000
8000
6000
4000
2000
0
0
50
100
150
200
250
300
Ce (ng/mL)
Peat Acetaminophen

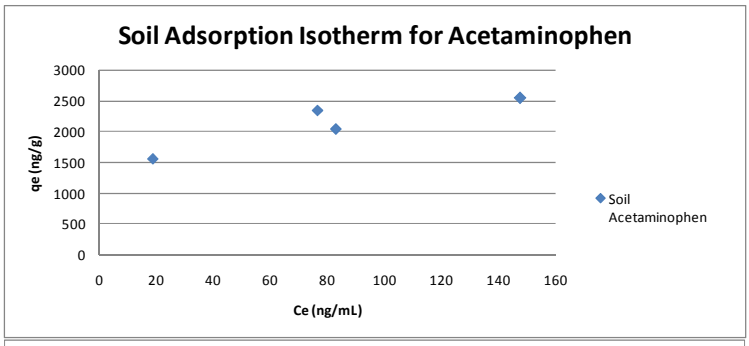

Peat Adsorption Isotherm for Caffeine
qe (ng/g)
14000
12000
10000
8000
6000
4000
2000
0
0
50
100
150
200
Ce (ng/mL)
Peat Caffeine

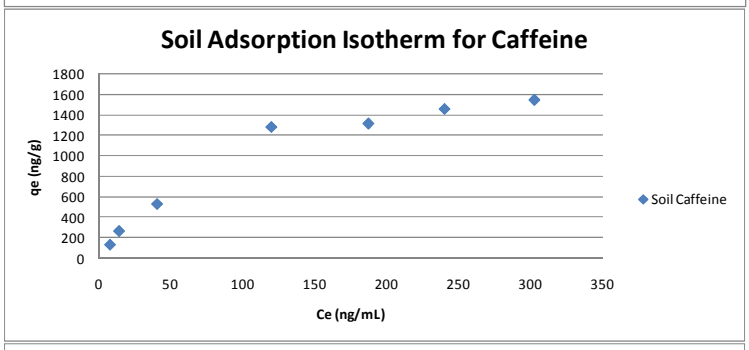

Peat Asorption Isotherm for Sulfamethoxazole
qe (ng/g)
16000
14000
12000
10000
8000
6000
4000
2000
0
0
50
100
150
200
Ce (ng/mL)
Peat Sulfamethoxazole

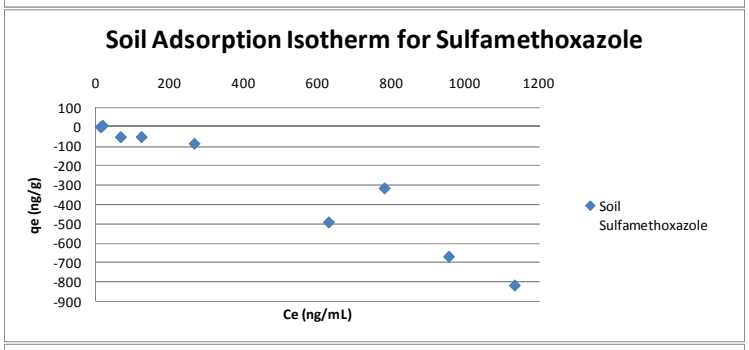

Peat Adsorption Isotherm for Fluoxetine
qe (ng/g)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
10
20
30
40
50
60
70
80
90
Ce (ng/mL)
Peat Fluoxetine

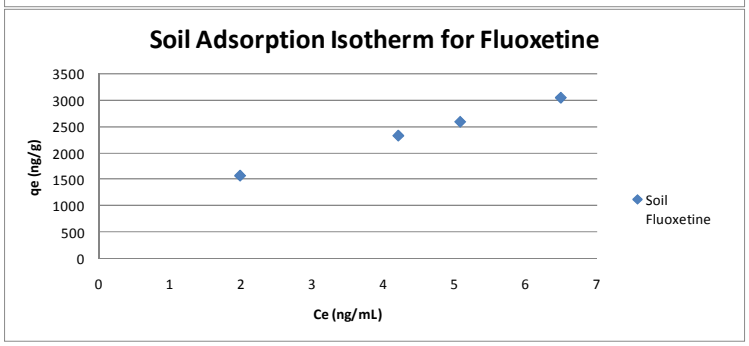

Peat Adsorption Isotherm for Carbamazepine
qe (ng/g)
16000
14000
12000
10000
8000
6000
4000
2000
0
0
20
40
60
80
100
120
140
160
Ce (ng/mL)
Peat Carbamazepine

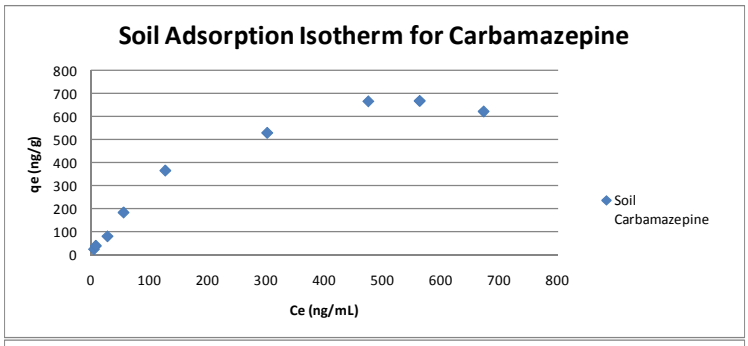

Peat Adsorption Isotherm for Progesterone
qe (ng/g)
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
20
40
60
80
100
120
140
160
180
Ce (ng/mL)
Peat Progesterone

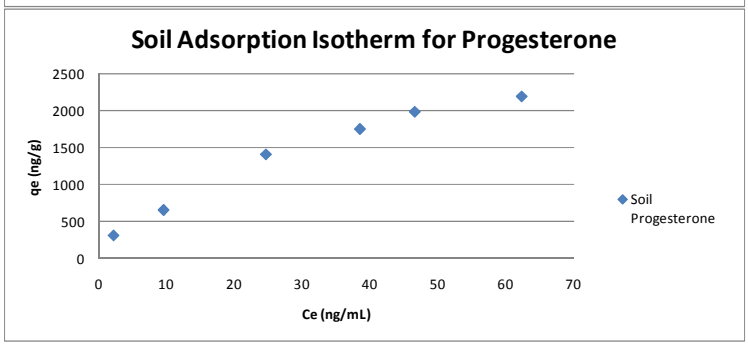

Soil Adsorption Isotherm for Acetaminophen
qe (ng/g)
3000
2500
2000
1500
1000
500
0
0 20 40 60 80 100 120 140 160
Ce (ng/mL)
Soil Acetaminophen


Soil Adsorption Isotherm for Caffeine
qe (ng/g)
1800
1600
1400
1200
1000
800
600
400
200
0
0 50 100 150 200 250 300 350
Ce (ng/mL)
Soil Caffeine


Soil Adsorption Isotherm for Sulfamethoxazole
0 200 400 600 800 1000 1200
100
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
qe (ng/g)
Ce (ng/mL)
Soil Sulfamethoxazole


Soil Adsorption Isotherm for Fluoxetine
qe (ng/g)
3500
3000
2500
2000
1500
1000
500
0
0 1 2 3 4 5 6 7
Ce (ng/mL)
Soil Fluoxetine

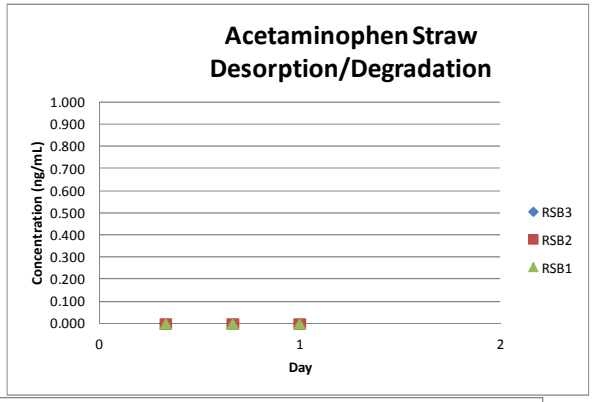

Soil Adsorption Isotherm for Carbamazepine
800
700
600
500
400
300
200
100
0
qe (ng/g)
0
100
200
300
400
500
600
700
800
Ce (ng/mL)
Soil Carbamazepine

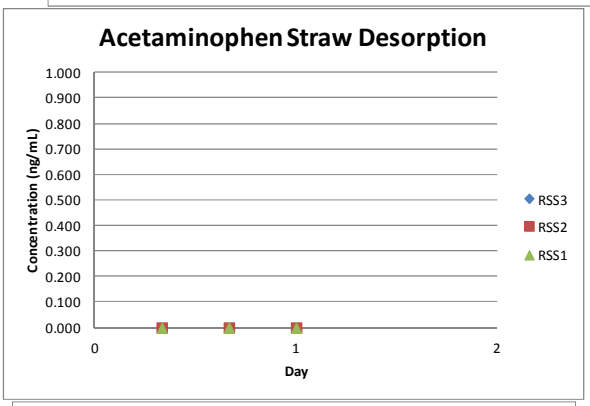

Soil Adsorption Isotherm for Progesterone
2500
2000
1500
1000
500
0
qe (ng/g)
0
10
20
30
40
50
60
70
Ce (ng/mL)
Soil Progesterone

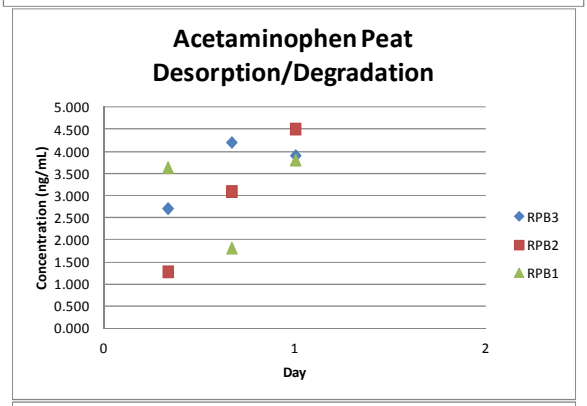
I Tabulated Freundlich Isotherm

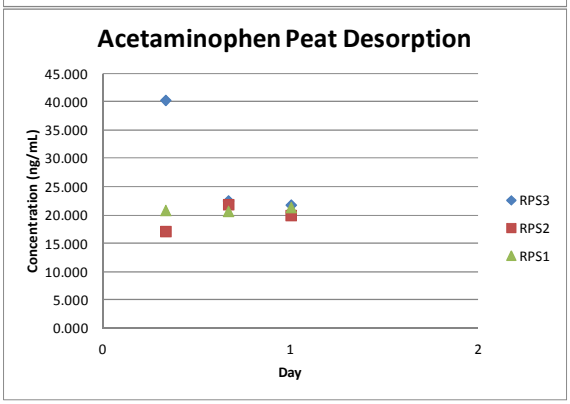
Sorbent	Sorbate	Linear Equation	Correlation Coefficient (R^2)	Predicted vs. Observed Equation	Correlation Coefficient (R^2)	Residuals Equation	Correlation Coefficient (R^2)
Charred Straw	Acetaminophen	y = 1.133x + 2.925	0.907	y = 1.000x - 0.001	0.907	y = -0.000x - 6E-05	2.00E-06
Charred Straw	Caffeine	y = 0.565x + 3.852	0.32	y = 1.000x - 0.002	0.32	y = -0.000x - 0.000	3.00E-07
Charred Straw	Sulfamethoxazole	y = 1.165x + 0.772	0.883	y = 1.000x + 0.000	0.883	y = -0.000x - 0.000	3.00E-07
Charred Straw	Fluoxetine	y = 0.928x + 3.585	0.809	y = 1.000x - 0.003	0.809	y = -0.000x - 0.000	4.00E-06
Charred Straw	Carbamazepine	y = 0.427x + 3.976	0.846	y = 1.001x - 0.005	0.846	y = -0.000x - 5E-05	1.00E-05
Charred Straw	Progesterone	y = 1.859x + 2.259	0.823	y = 1.000x + 0.000	0.823	y = -0.000x - 0.000	2.00E-08
Peat	Acetaminophen	y = 0.937x + 1.713	0.993	y = 1.000x + 0.542	0.993	y = -6E-05x - 0.542	7.00E-07
Peat	Caffeine	y = 1.050x + 1.725	0.962	y = 1x - 1E-05	0.981	y = -1E-06x + 1E-05	1.00E-10
Peat	Sulfamethoxazole	y = 0.802x + 2.420	0.964	y = 1.000x - 0.000	0.92	y = -0.000x - 0.000	2.00E-06
Peat	Fluoxetine	y = 0.771x + 2.769	0.974	y = 0.963x - 0.016	0.98	y = 0.045x + 0.089	0.023
Peat	Carbamazepine	y = 0.735x + 2.635	0.987	y = 1.000x - 0.001	0.978	y = -0.000x - 0.000	2.00E-05
Peat	Progesterone	y = 0.244x + 3.465	0.181	y = 1.001x - 0.003	0.644	y = -0.000x - 0.000	4.00E-06
Soil	Acetaminophen	y = 0.231x + 2.901	0.91	y = 1.000x - 0.001	0.91	y = -0.000x - 0.000	5.00E-06
Soil	Caffeine	y = 0.663x + 1.616	0.971	y = 1.000x + 0.000	0.971	y = -6E-05x - 0.000	3.00E-07
Soil	Sulfamethoxazole						
Soil	Fluoxetine	y = 0.550x + 3.030	0.997	y = 1.001x - 0.004	0.997	y = -0.000x - 0.000	0.001
Soil	Carbamazepine	y = 0.687x + 0.973	0.977	y = 1.000x - 0.000	0.977	y = -0.000x - 0.000	3.00E-05
Soil	Progesterone	y = 0.617x + 2.256	0.992	y = 1.000x - 0.000	0.992	y = -0.000x - 0.000	1.00E-05

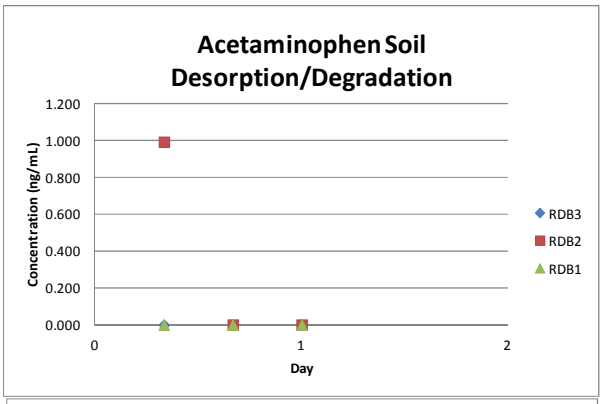
J Desorption

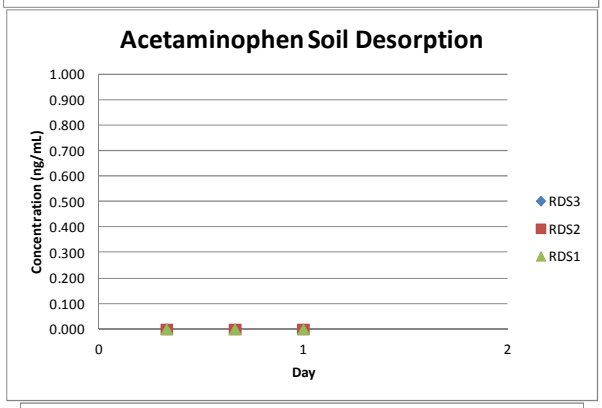


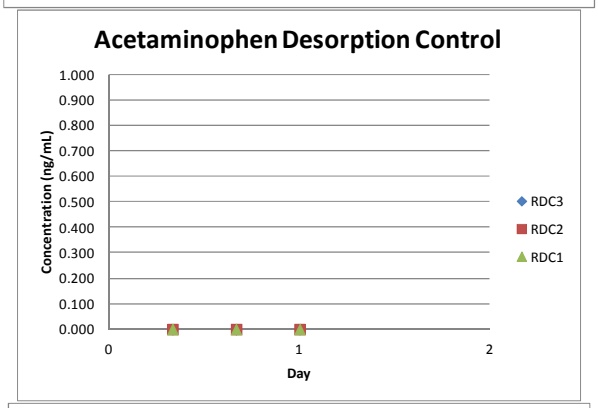


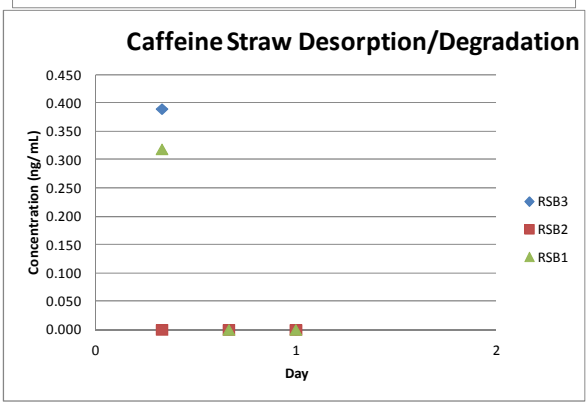


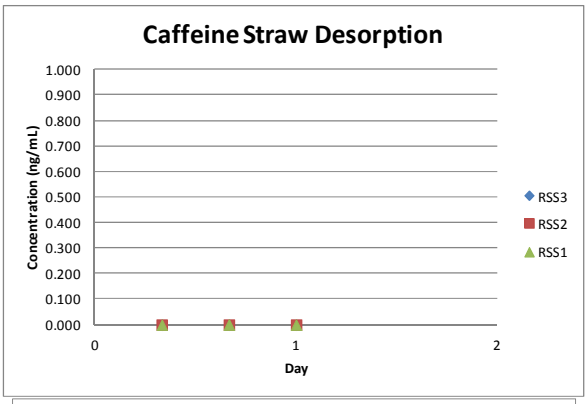


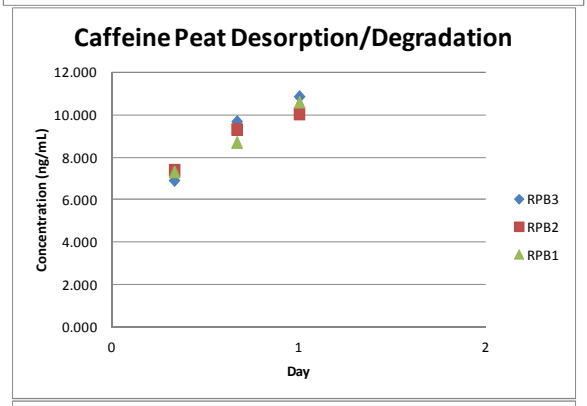

Acetaminophen Soil Desorption/Degradation
Concentration (ng/mL)
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0
1
2
Day
RDB3
RDB2
RDB1

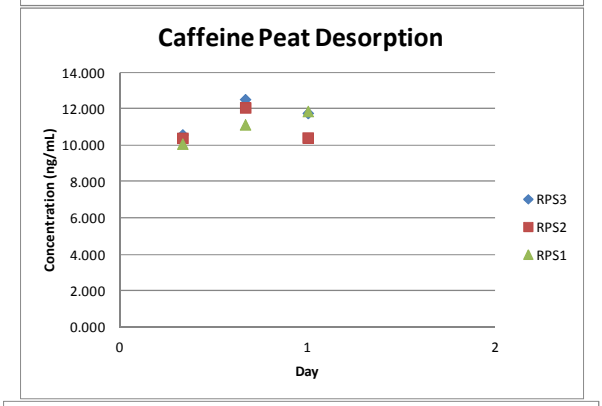

Acetaminophen Soil Desorption
Concentration (ng/mL)
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
1
2
Day
RDS3
RDS2
RDS1

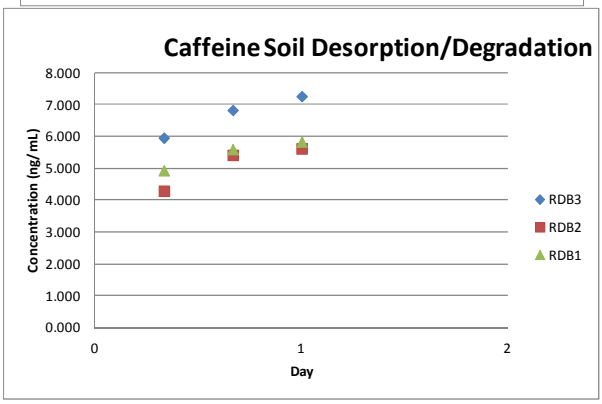

Acetaminophen Desorption Control
Concentration (ng/mL)
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
1
2
Day
RDC3
RDC2
RDC1

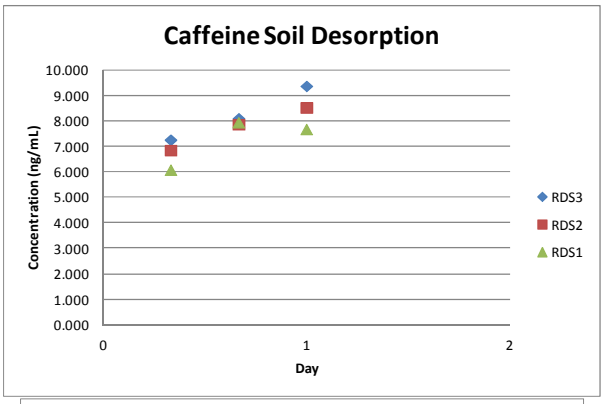

Caffeine Straw Desorption/Degradation
Concentration (ng/mL)
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0
1
2
Day
RSB3
RSB2
RSB1

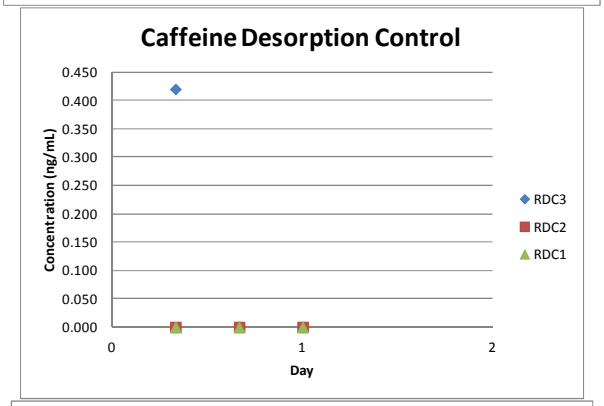

Caffeine Straw Desorption
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
Concentration (ng/mL)
0
1
2
Day
RSS3
RSS2
RSS1

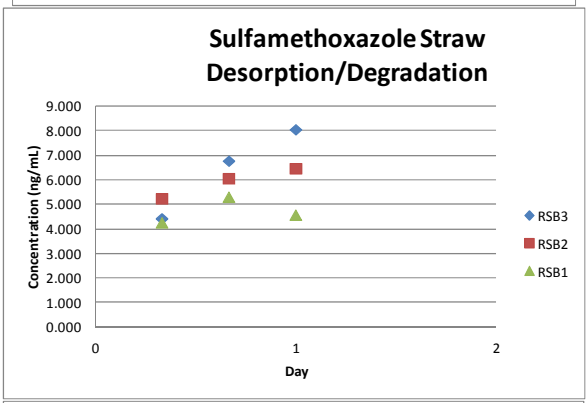

Caffeine Peat Desorption/Degradation
12.000
10.000
8.000
6.000
4.000
2.000
0.000
Concentration (ng/mL)
0
1
2
Day
RPB3
RPB2
RPB1

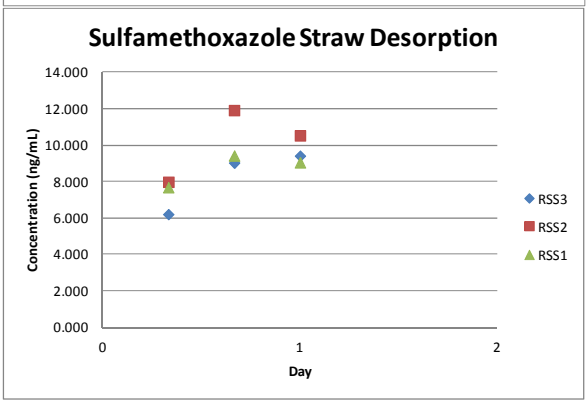

Caffeine Peat Desorption
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
Concentration (ng/mL)
0
1
2
Day
RPS3
RPS2
RPS1

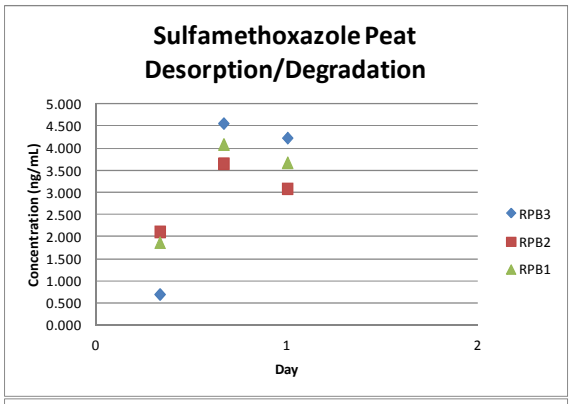

Caffeine Soil Desorption/Degradation
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
Concentration (ng/mL)
0
1
2
Day
RDB3
RDB2
RDB1

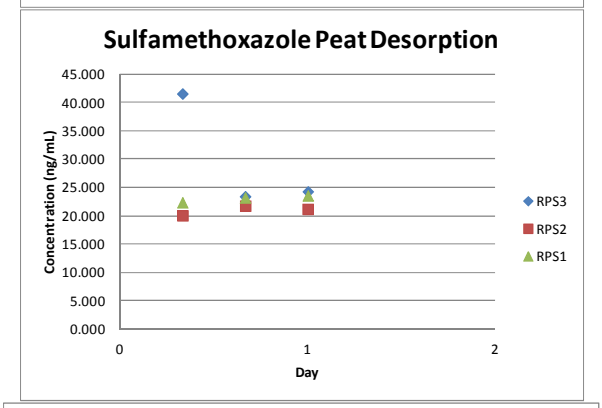

Caffeine Soil Desorption
10.000
9.000
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
Concentration (ng/mL)
0
1
2
Day
RDS3
RDS2
RDS1

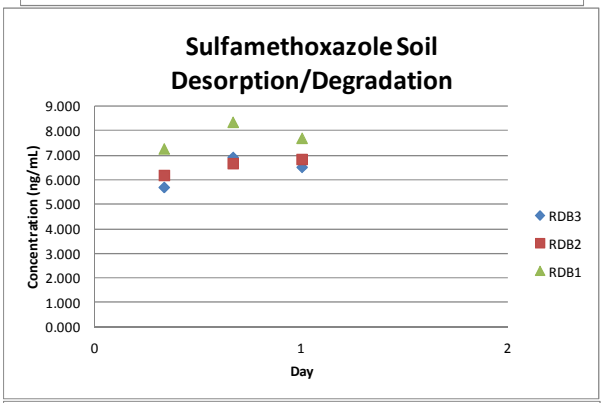

Caffeine Desorption Control
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.050
0.000
Concentration (ng/mL)
0
1
2
Day
RDC3
RDC2
RDC1

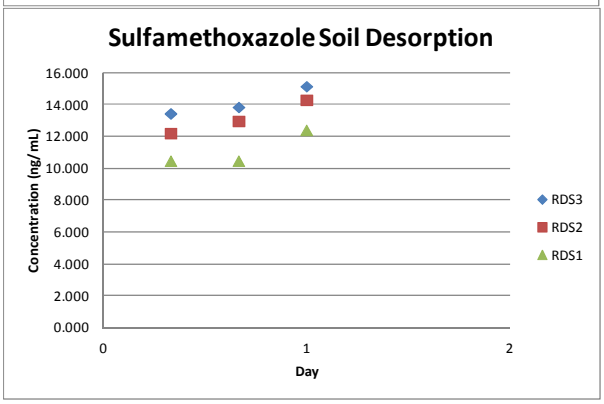

Sulfamethoxazole Straw Desorption/Degradation
9.000
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
Concentration (ng/mL)
0
1
2
Day
RSB3
RSB2
RSB1

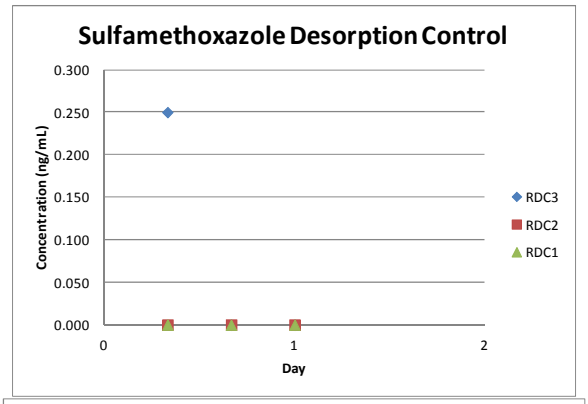

Sulfamethoxazole Straw Desorption
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
Concentration (ng/mL)
0
1
2
Day
RSS3
RSS2
RSS1

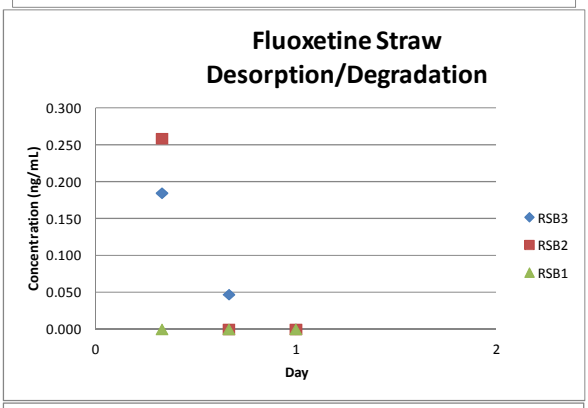

Sulfamethoxazole Peat Desorption/Degradation
Concentration (ng/mL)
5.000
4.500
4.000
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
0
1
2
Day
RPB3
RPB2
RPB1

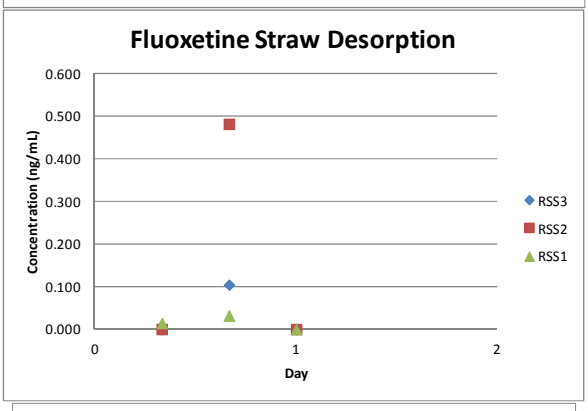

Sulfamethoxazole Peat Desorption
Concentration (ng/mL)
45.000
40.000
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0.000
0
1
2
Day
RPS3
RPS2
RPS1

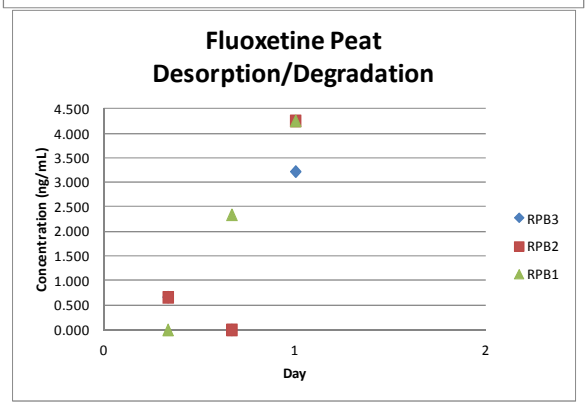

Sulfamethoxazole Soil Desorption/Degradation
Concentration (ng/mL)
9.000
8.000
7.000
6.000
5.000
4.000
3.000
2.000
1.000
0.000
0
1
2
Day
RDB3
RDB2
RDB1

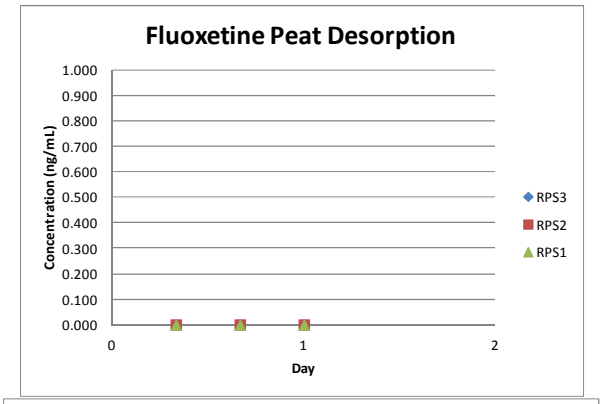

Sulfamethoxazole Soil Desorption
Concentration (ng/mL)
16.000
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
0
1
2
Day
RDS3
RDS2
RDS1

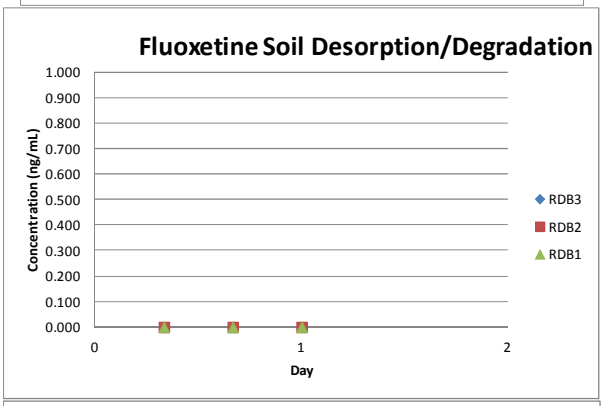

Sulfamethoxazole Desorption Control
Concentration (ng/mL)
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0
1
2
Day
RDC3
RDC2
RDC1

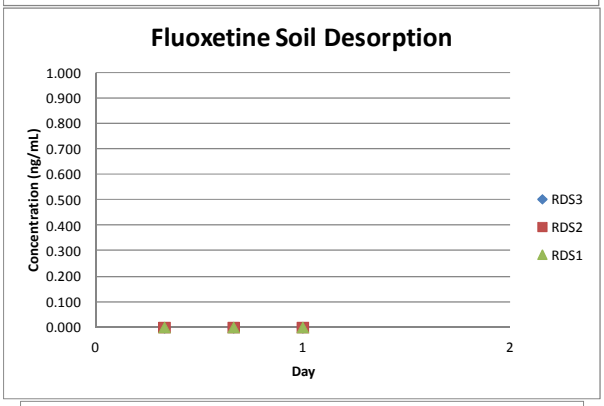

Fluoxetine Straw Desorption/Degradation
Concentration (ng/mL)
0.300
0.250
0.200
0.150
0.100
0.050
0.000
0
1
2
Day
RSB3
RSB2
RSB1

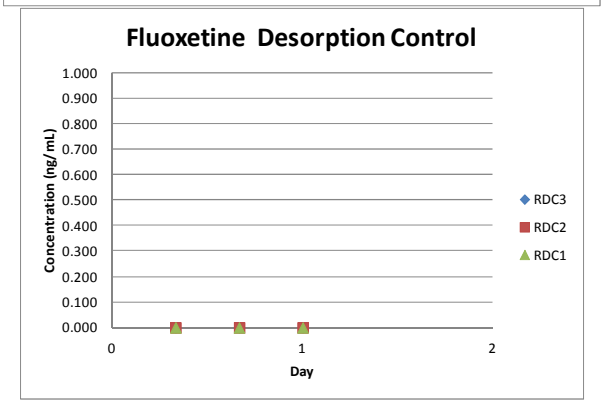

Fluoxetine Straw Desorption
Concentration (ng/mL)
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
1
2
Day
RSS3
RSS2
RSS1

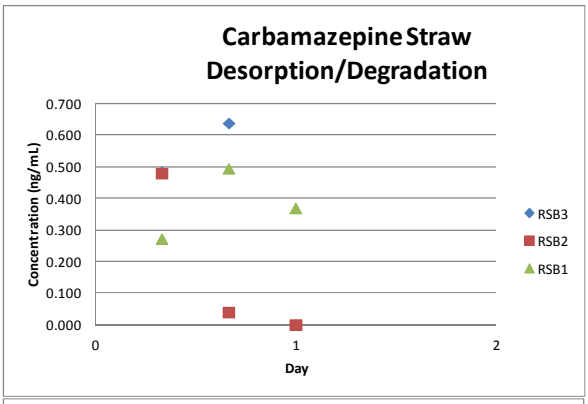

Fluoxetine Peat Desorption/Degradation
Concentration (ng/mL)
4.500
4.000
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
0
1
2
Day
RPB3
RPB2
RPB1

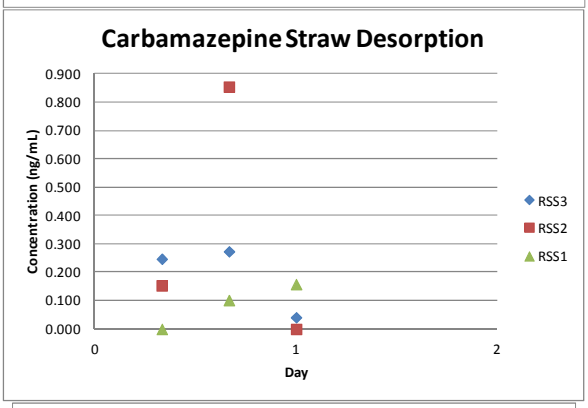

Fluoxetine Peat Desorption
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
Concentration (ng/mL)
0
1
2
Day
RPS3
RPS2
RPS1

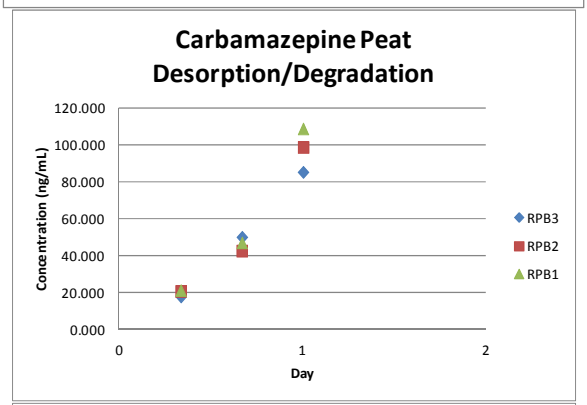

Fluoxetine Soil Desorption/Degradation
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
Concentration (ng/mL)
0
1
2
Day
RDB3
RDB2
RDB1

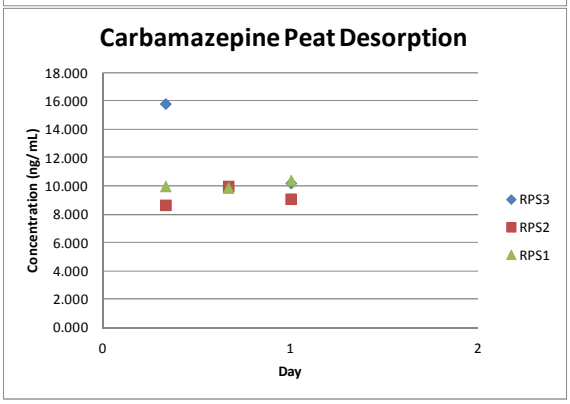

Fluoxetine Soil Desorption
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
Concentration (ng/mL)
0
1
2
Day
RDS3
RDS2
RDS1

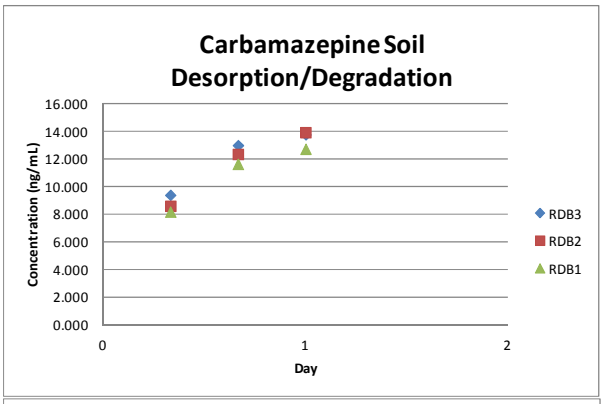

Fluoxetine Desorption Control
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
Concentration (ng/mL)
0
1
2
Day
RDC3
RDC2
RDC1

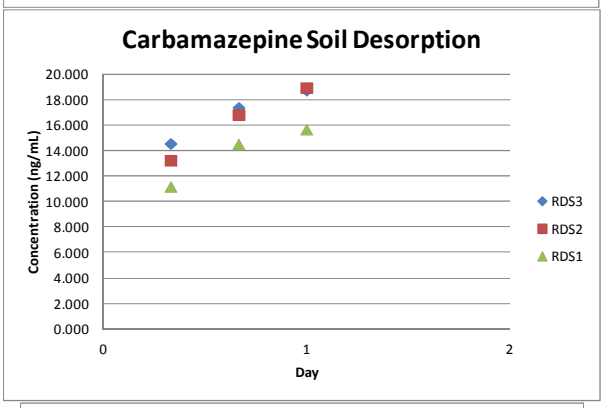

Carbamazepine Straw Desorption/Degradation
Concentration (ng/mL)
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
1
2
Day
RSB3
RSB2
RSB1

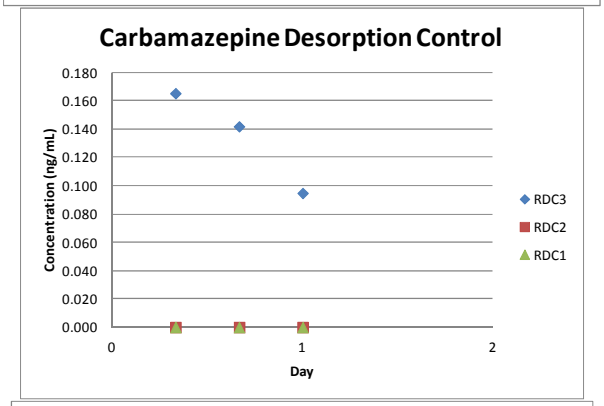

Carbamazepine Straw Desorption
Concentration (ng/mL)
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
1
2
Day
RSS3
RSS2
RSS1

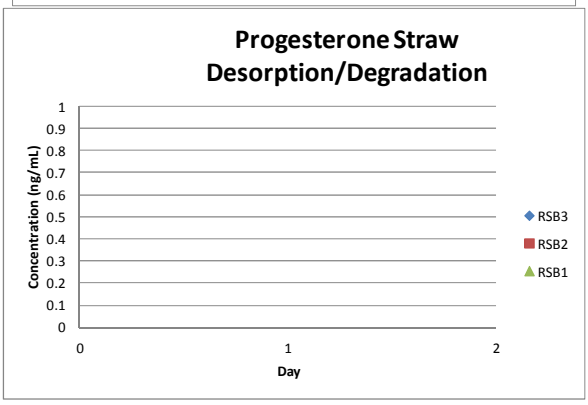

Carbamazepine Peat Desorption/Degradation
Concentration (ng/mL)
120.000
100.000
80.000
60.000
40.000
20.000
0.000
0
1
2
Day
RPB3
RPB2
RPB1

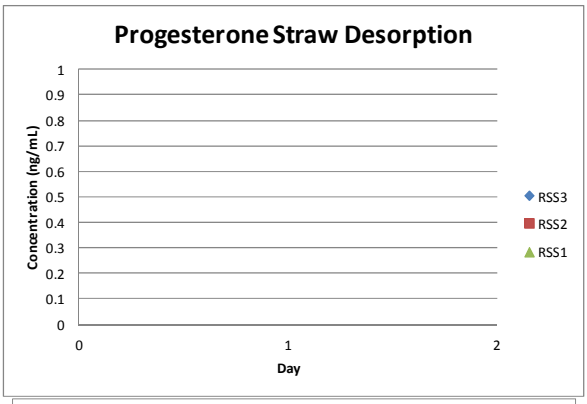

Carbamazepine Peat Desorption
Concentration (ng/mL)
18.000
16.000
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
0
1
2
Day
RPS3
RPS2
RPS1

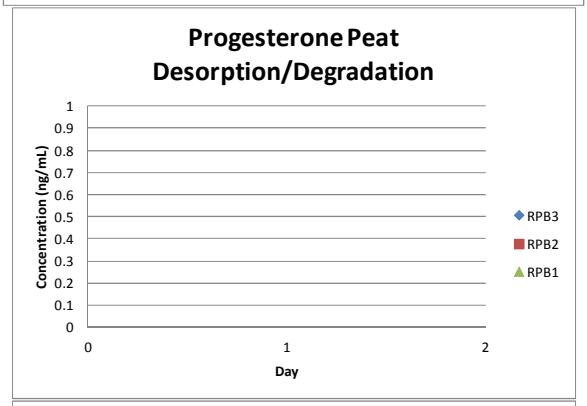

Carbamazepine Soil Desorption/Degradation
Concentration (ng/mL)
16.000
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
0
1
2
Day
RDB3
RDB2
RDB1

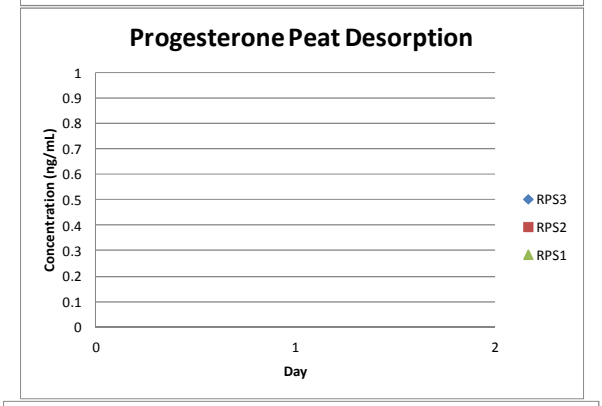

Carbamazepine Soil Desorption
Concentration (ng/mL)
20.000
18.000
16.000
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
0
1
2
Day
RDS3
RDS2
RDS1

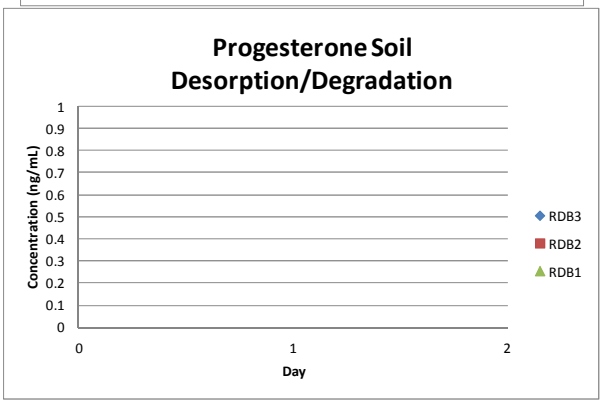

Carbamazepine Desorption Control
Concentration (ng/mL)
0.180
0.160
0.140
0.120
0.100
0.080
0.060
0.040
0.020
0.000
0
1
2
Day
RDC3
RDC2
RDC1

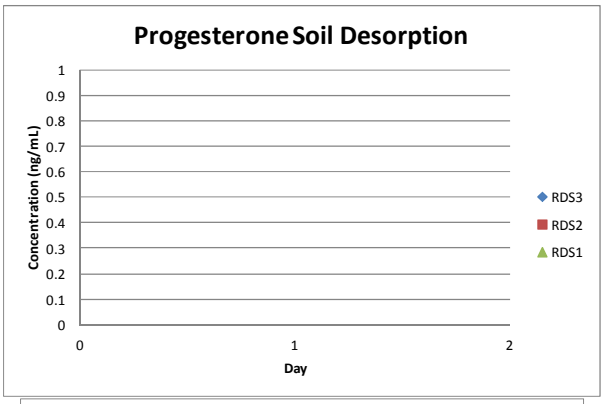

Progesterone Straw Desorption/Degradation
Concentration (ng/mL)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
Day
RSB3
RSB2
RSB1

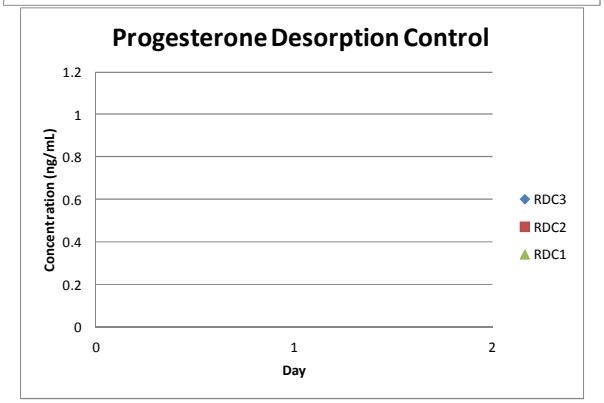

Progesterone Straw Desorption
Concentration (ng/mL)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
Day
RSS3
RSS2
RSS1


Progesterone Peat Desorption/Degradation
Concentration (ng/mL)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
Day
RPB3
RPB2
RPB1

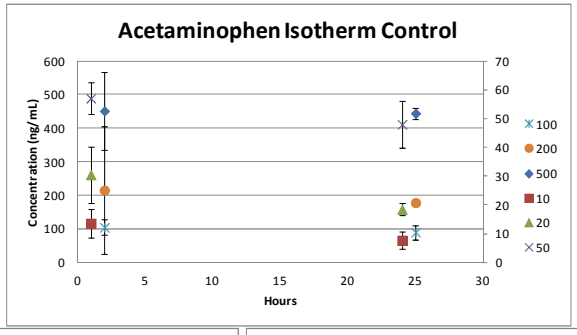

Progesterone Peat Desorption
Concentration (ng/mL)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
Day
RPS3
RPS2
RPS1

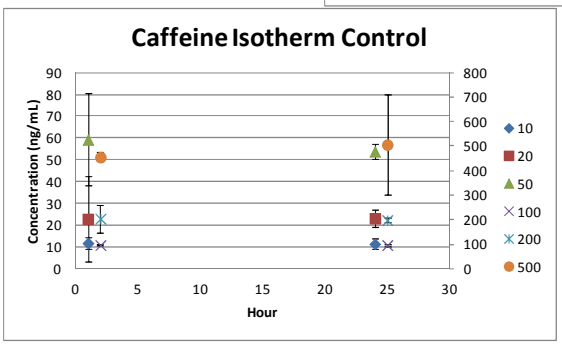

Progesterone Soil Desorption/Degradation
Concentration (ng/mL)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
Day
RDB3
RDB2
RDB1

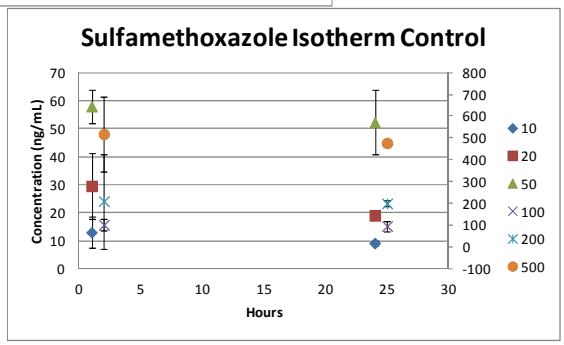


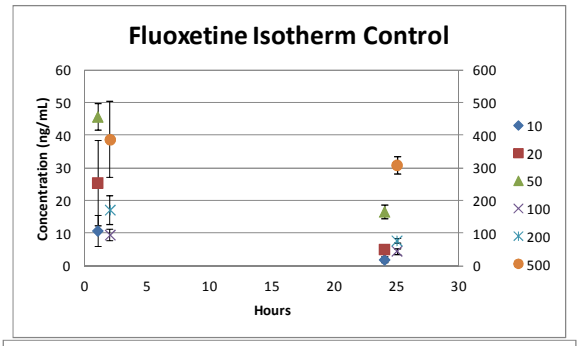


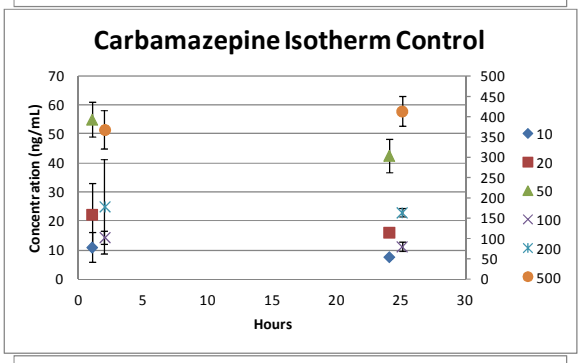
K Control Isotherms

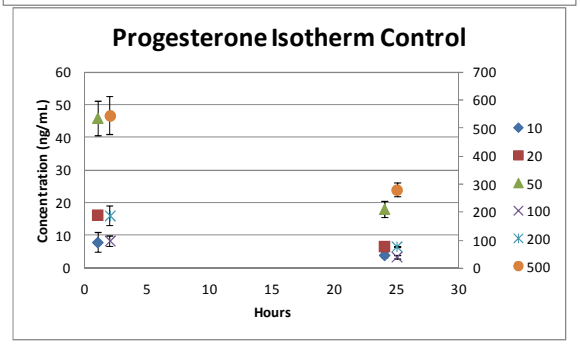




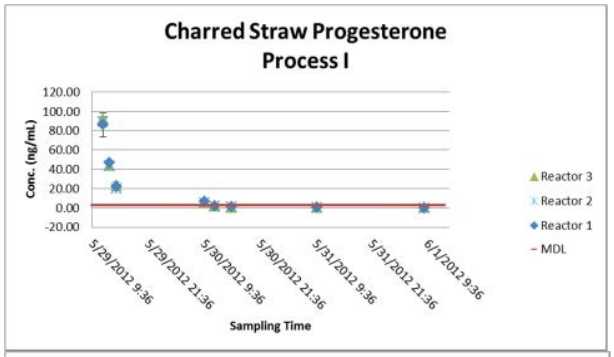


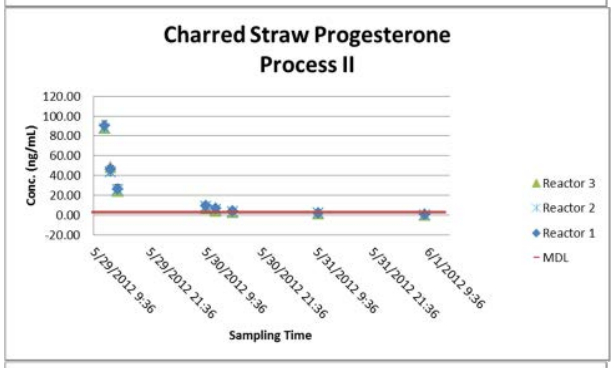

Fluoxetine Isotherm Control
Concentration (ng/mL)
Hours
10
20
50
100
200
500

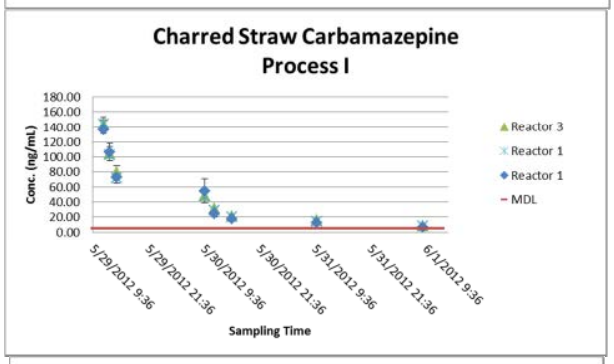

Carbamazepine Isotherm Control
Concentration (ng/mL)
Hours
10
20
50
100
200
500

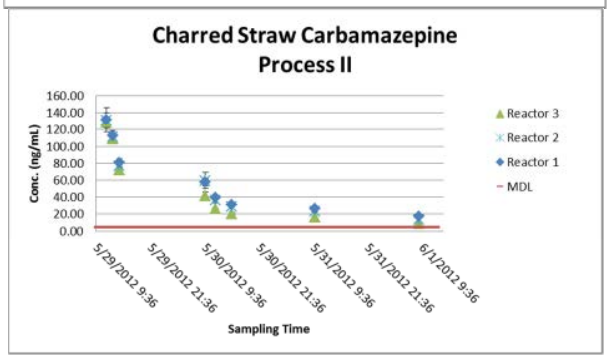

Progesterone Isotherm Control
Concentration (ng/mL)
Hours
10
20
50
100
200
500

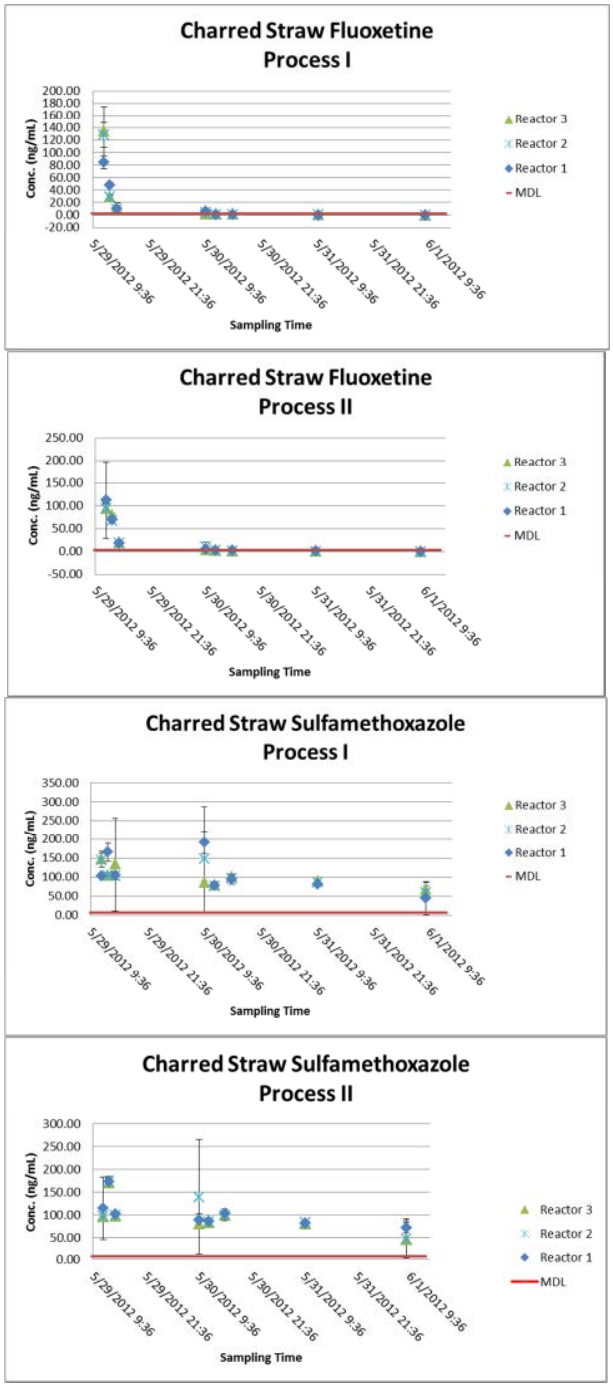
L Batch Reactors

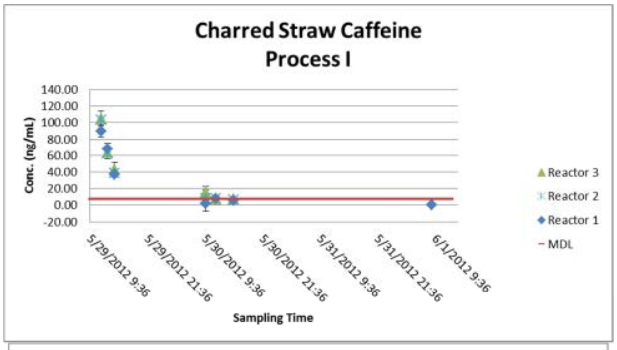


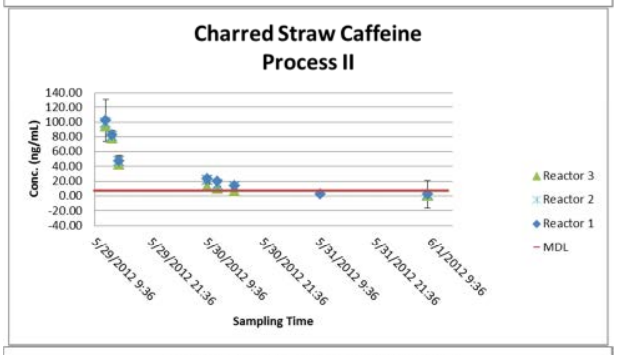


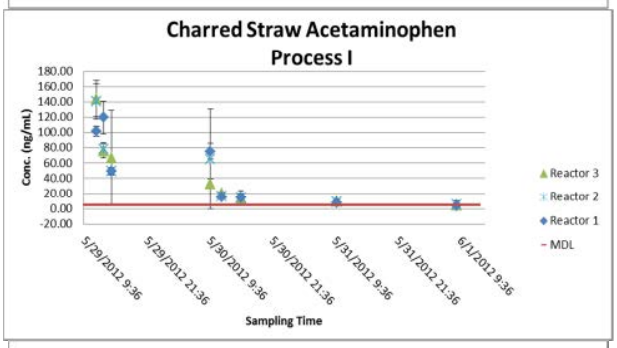


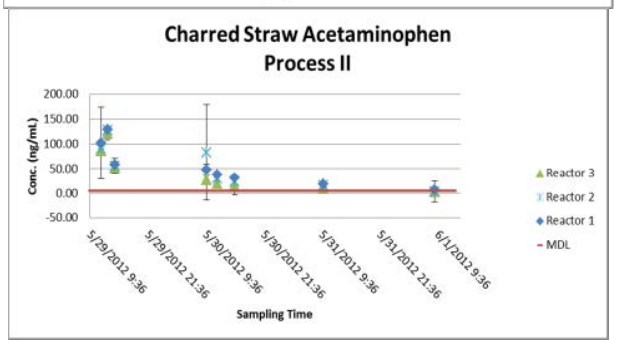


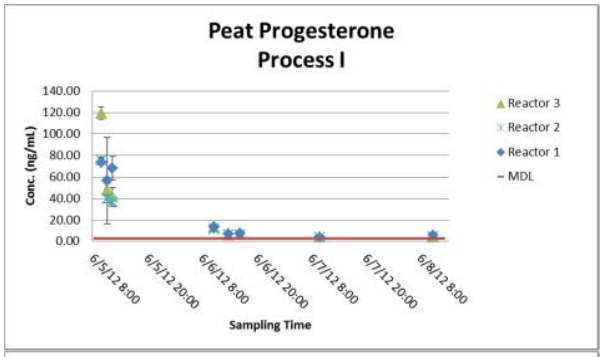

Charred Straw Fluoxetine
Process I
Conc. (ng/mL)
200.00
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
-20.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL
Charred Straw Fluoxetine
Process II
Conc. (ng/mL)
250.00
200.00
150.00
100.00
50.00
0.00
-50.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL
Charred Straw Sulfamethoxazole
Process I
Conc. (ng/mL)
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL
Charred Straw Sulfamethoxazole
Process II
Conc. (ng/mL)
300.00
250.00
200.00
150.00
100.00
50.00
0.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

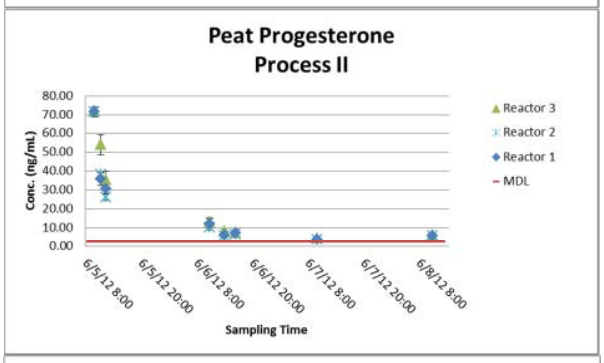

Charred Straw Caffeine
Process I
Conc. (ng/mL)
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
-20.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

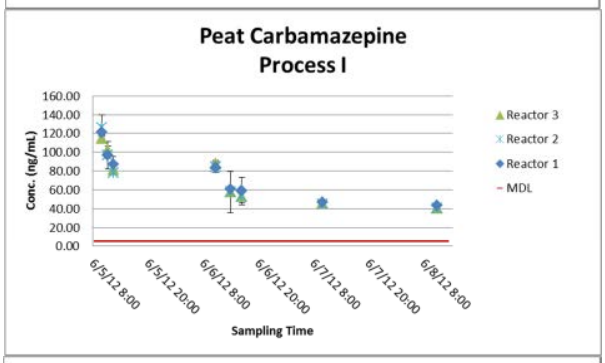

Charred Straw Caffeine
Process II
Conc. (ng/mL)
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
-20.00
-40.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

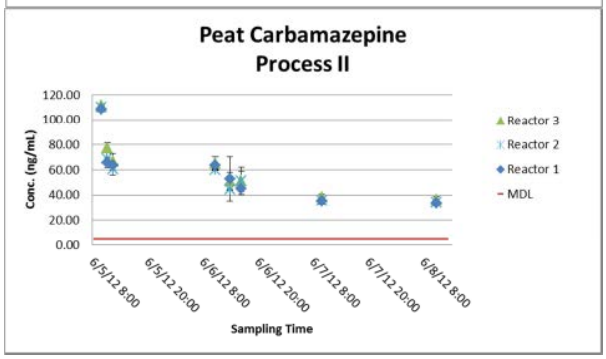

Charred Straw Acetaminophen
Process I
Conc. (ng/mL)
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
-20.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

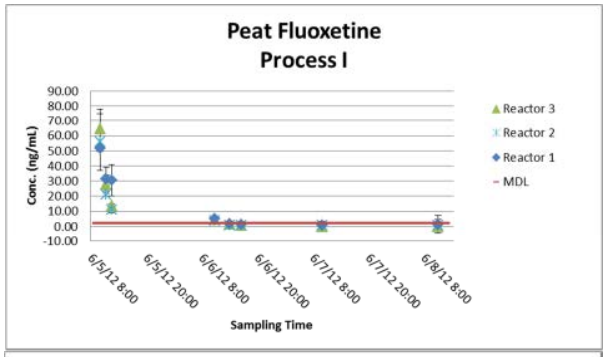

Charred Straw Acetaminophen
Process II
Conc. (ng/mL)
200.00
150.00
100.00
50.00
0.00
-50.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

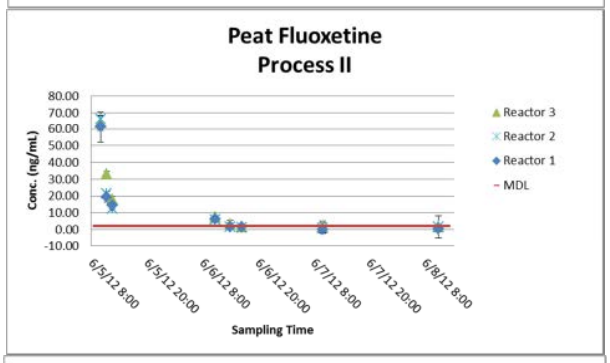

Peat Progesterone
Process I
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

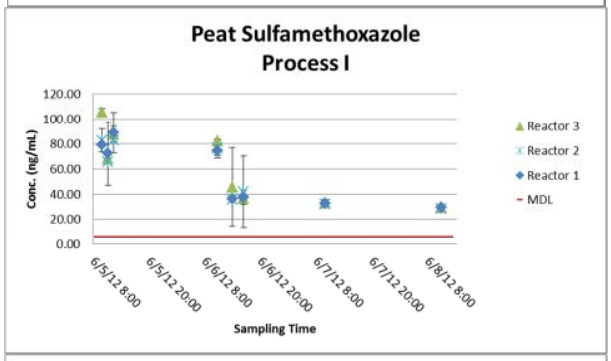

Peat Progesterone
Process II
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

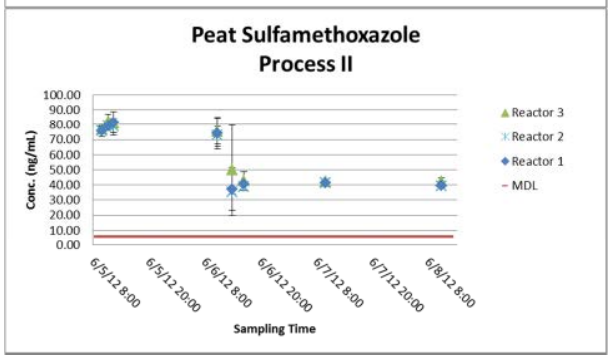

Peat Carbamazepine
Process I
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

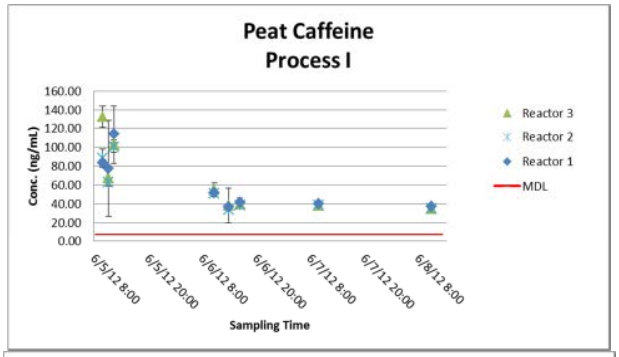

Peat Carbamazepine
Process II
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

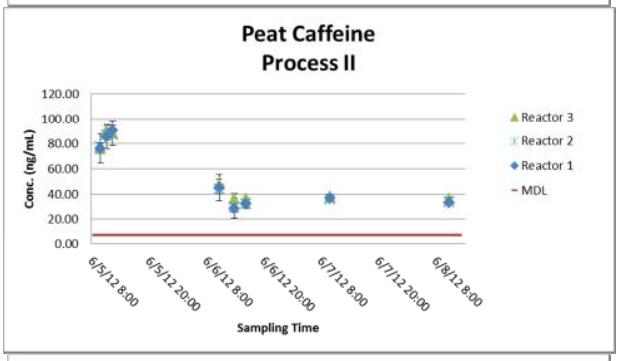

Peat Fluoxetine
Process I
Conc. (ng/mL)
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

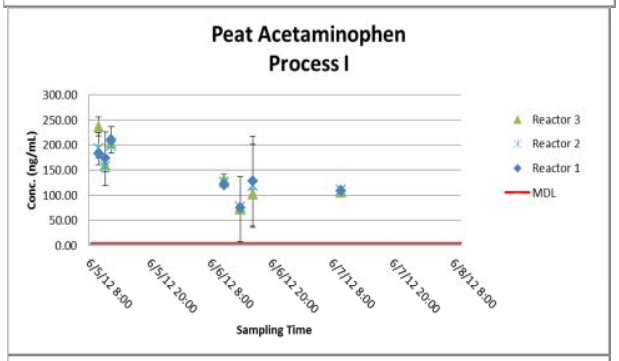

Peat Fluoxetine
Process II
Conc. (ng/mL)
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

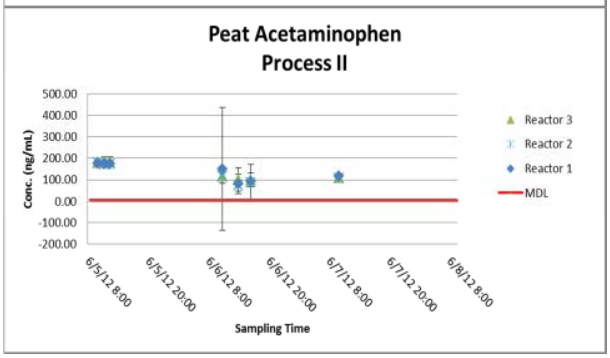

Peat Sulfamethoxazole
Process I
Conc. (ng/mL)
120.00
100.00
80.00
60.00
40.00
20.00
0.00
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

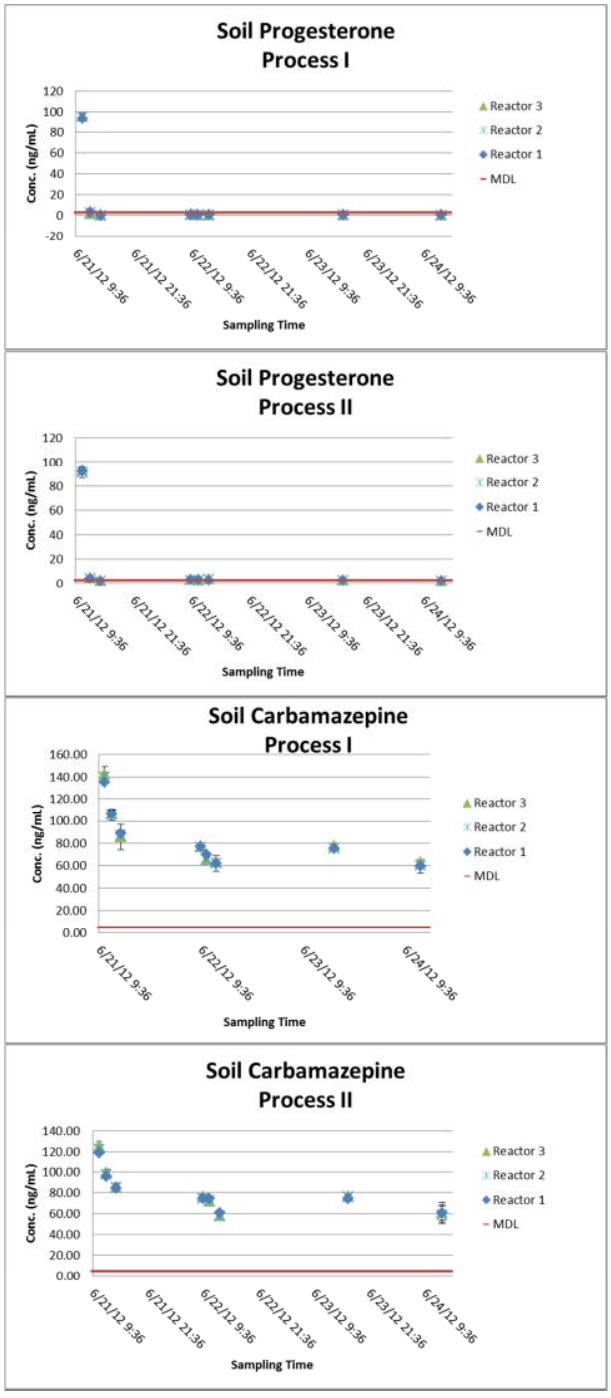

Peat Sulfamethoxazole
Process II
Conc. (ng/mL)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

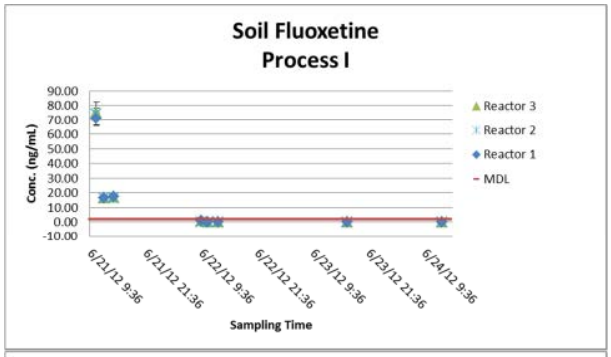

Peat Caffeine
Process I
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

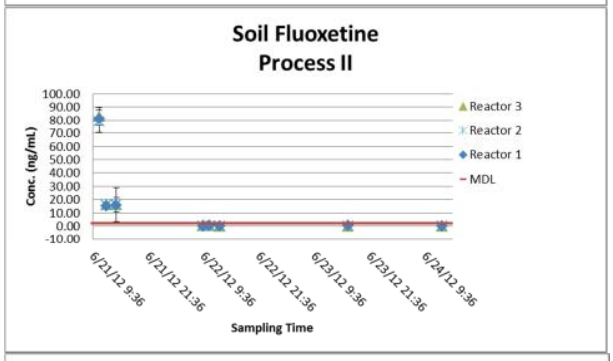

Peat Caffeine
Process II
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

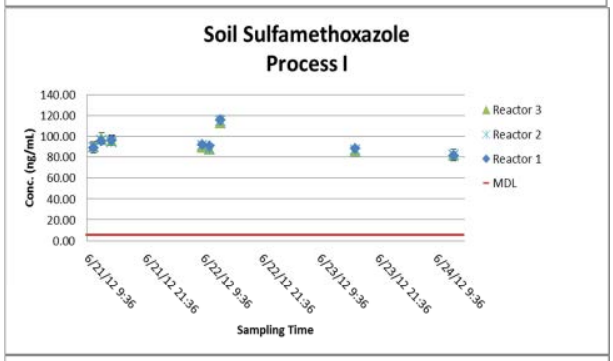

Peat Acetaminophen
Process I
300.00
250.00
200.00
150.00
100.00
50.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

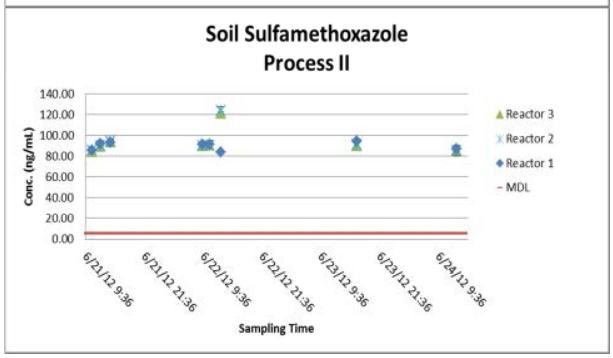

Peat Acetaminophen
Process II
500.00
400.00
300.00
200.00
100.00
0.00
-100.00
-200.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

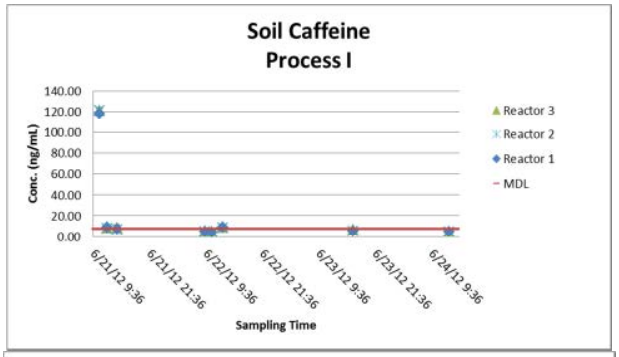

Soil Progesterone
Process I
Conc. (ng/mL)
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL
Soil Progesterone
Process II
Conc. (ng/mL)
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL
Soil Carbamazepine
Process I
Conc. (ng/mL)
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL
Soil Carbamazepine
Process II
Conc. (ng/mL)
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

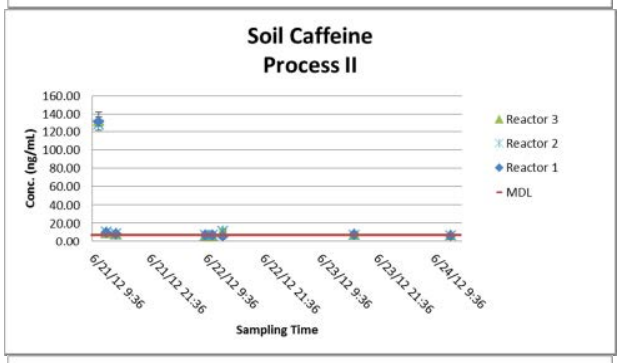

Soil Fluoxetine
Process I
Conc. (ng/mL)
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

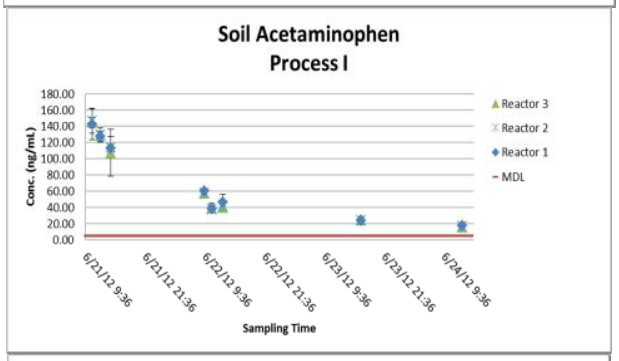

Soil Fluoxetine
Process II
Conc. (ng/mL)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

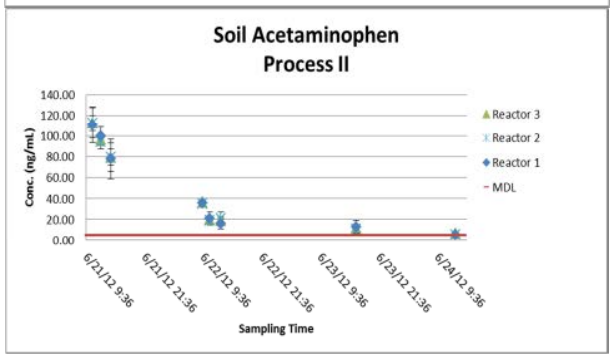

Soil Sulfamethoxazole
Process I
Conc. (ng/mL)
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

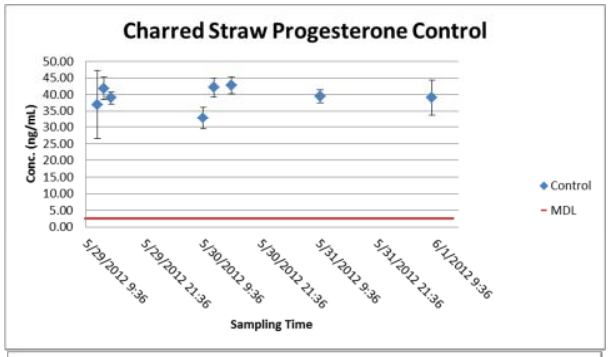

Soil Sulfamethoxazole
Process II
Conc. (ng/mL)
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

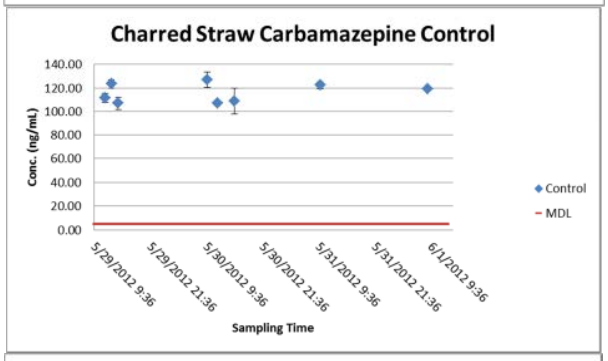

Soil Caffeine
Process I
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

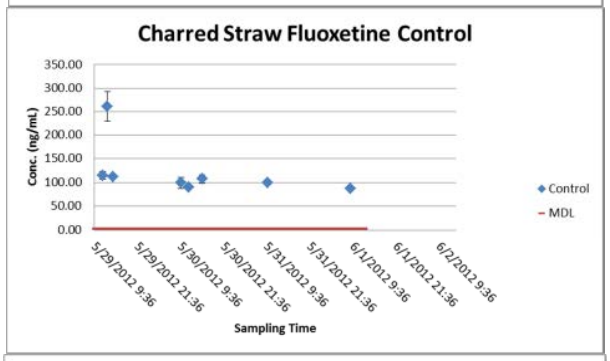

Soil Caffeine
Process II
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

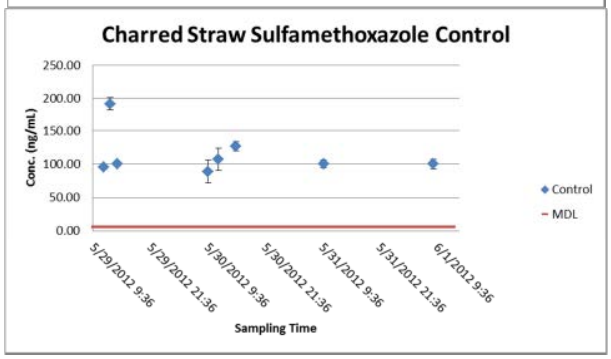

Soil Acetaminophen
Process I
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

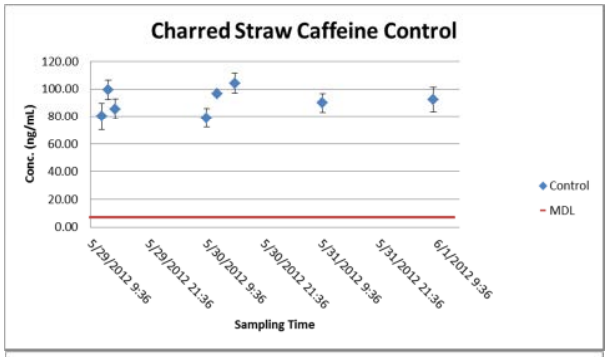

Soil Acetaminophen
Process II
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Reactor 3
Reactor 2
Reactor 1
MDL

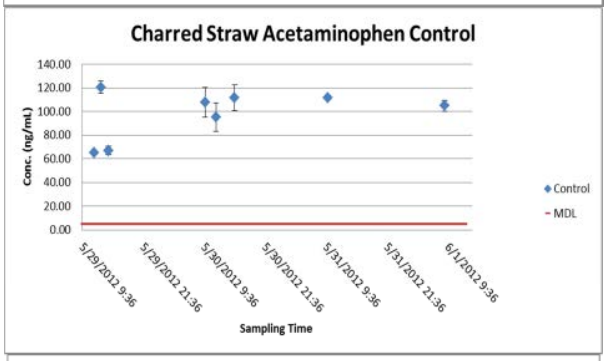

Charred Straw Progesterone Control
Conc. (ng/mL)
50.00
45.00
40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Control
MDL

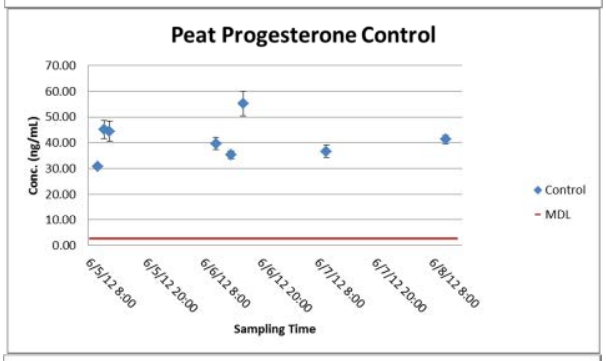

Charred Straw Carbamazepine Control
Conc. (ng/mL)
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Control
MDL

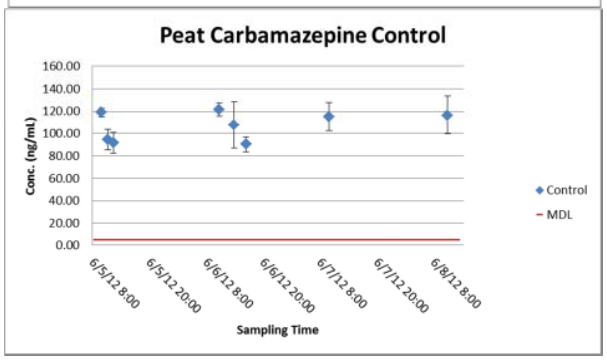

Charred Straw Fluoxetine Control
Conc. (ng/mL)
350.00
300.00
250.00
200.00
150.00
100.00
50.00
0.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
6/1/2012 21:36
6/2/2012 9:36
Sampling Time
Control
MDL

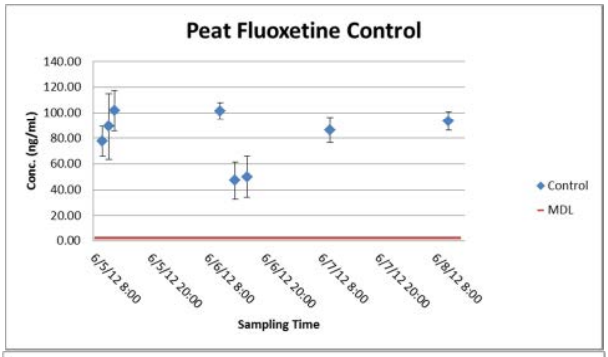

Charred Straw Sulfamethoxazole Control
Conc. (ng/mL)
250.00
200.00
150.00
100.00
50.00
0.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Control
MDL

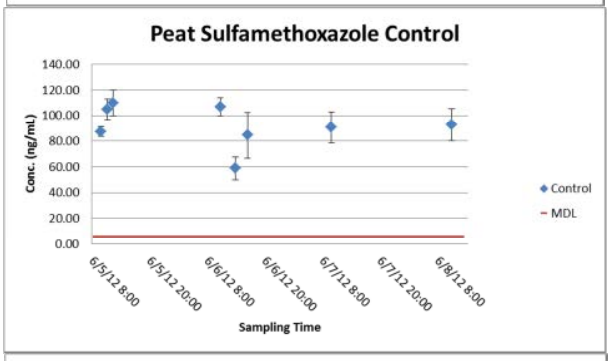

Charred Straw Caffeine Control
Conc. (ng/mL)
120.00
100.00
80.00
60.00
40.00
20.00
0.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Control
MDL

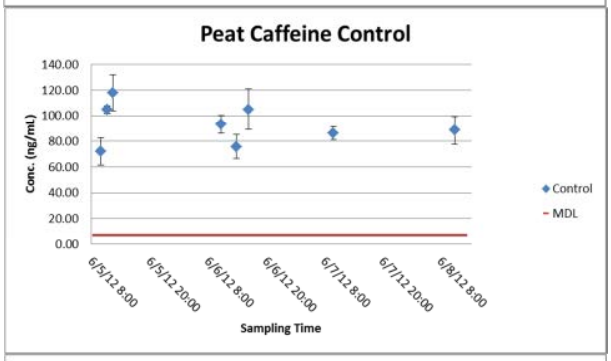

Charred Straw Acetaminophen Control
Conc. (ng/mL)
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
5/29/2012 9:36
5/29/2012 21:36
5/30/2012 9:36
5/30/2012 21:36
5/31/2012 9:36
5/31/2012 21:36
6/1/2012 9:36
Sampling Time
Control
MDL

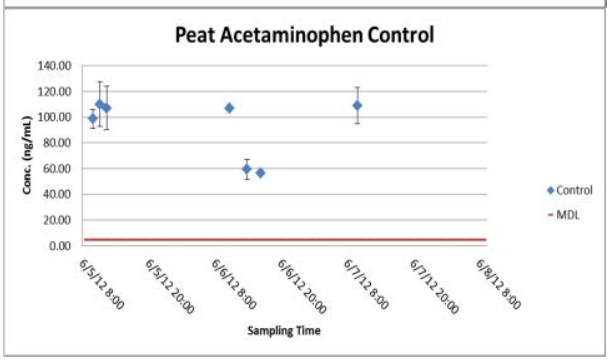

Peat Progesterone Control
Conc. (ng/mL)
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Control
MDL

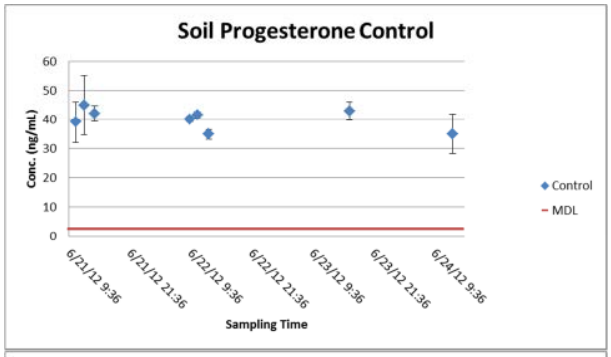

Peat Carbamazepine Control
Conc. (ng/mL)
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Control
MDL

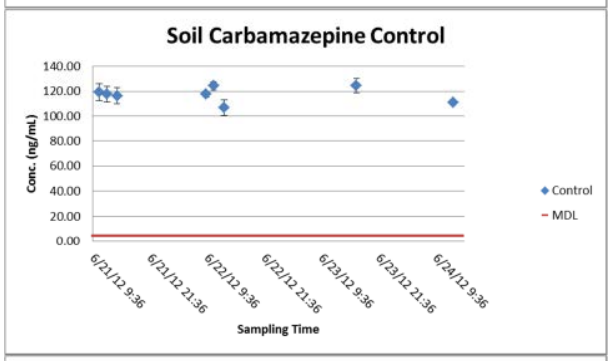

Peat Fluoxetine Control
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Control
MDL

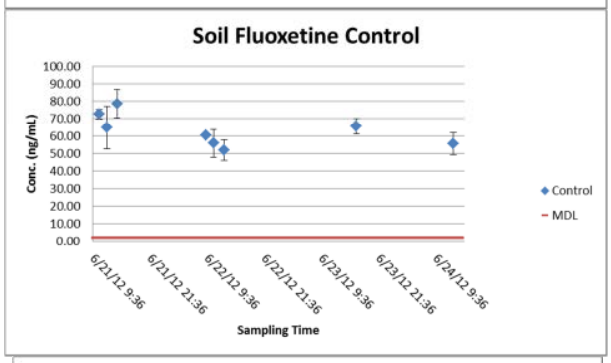

Peat Sulfamethoxazole Control
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Control
MDL

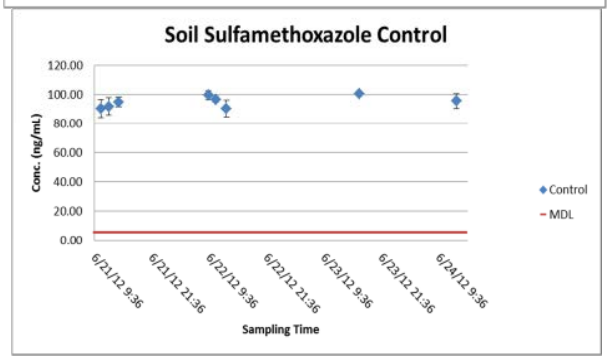

Peat Caffeine Control
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Control
MDL

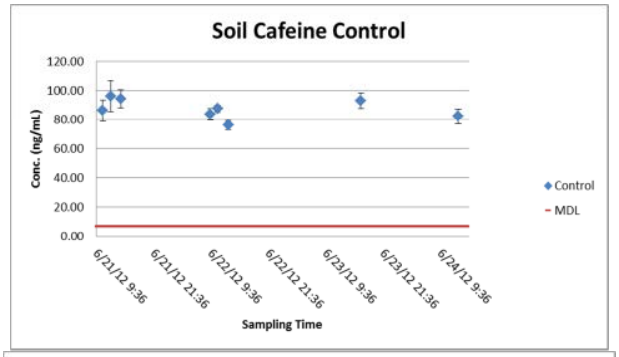

Peat Acetaminophen Control
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Conc. (ng/mL)
6/5/12 8:00
6/5/12 20:00
6/6/12 8:00
6/6/12 20:00
6/7/12 8:00
6/7/12 20:00
6/8/12 8:00
Sampling Time
Control
MDL

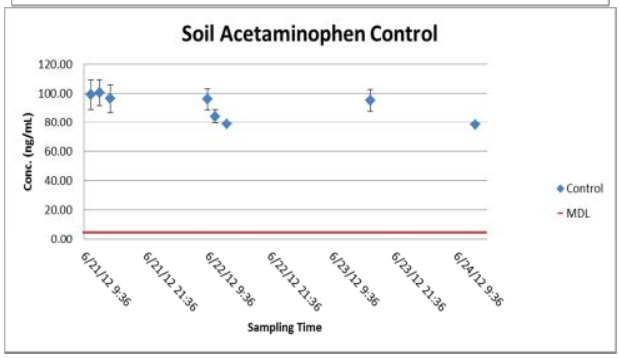

Soil Progesterone Control
Conc. (ng/mL)
60
50
40
30
20
10
0
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Control
MDL


Soil Carbamazepine Control
Conc. (ng/mL)
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Control
MDL

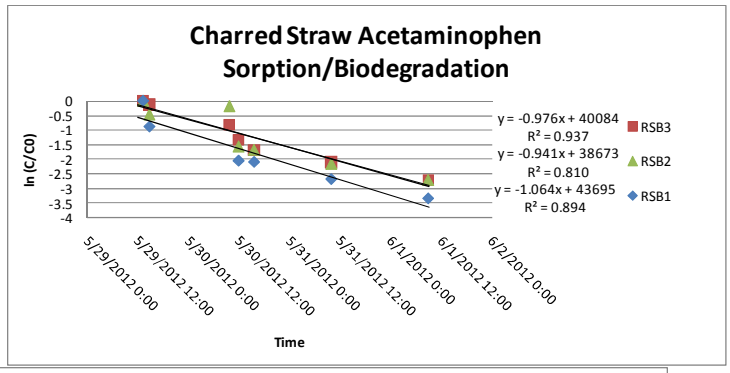

Soil Fluoxetine Control
Conc. (ng/mL)
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Control
MDL

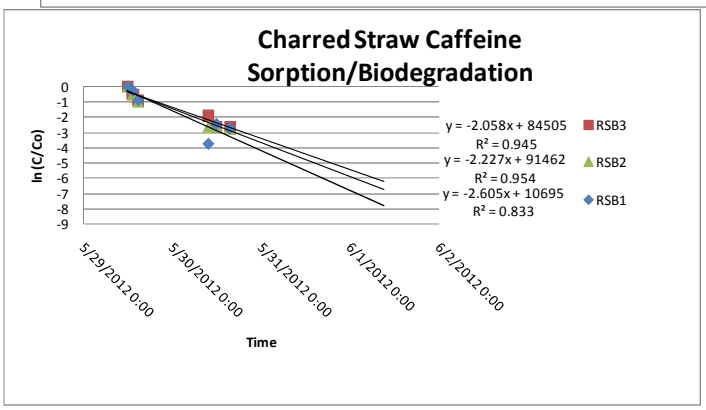

Soil Sulfamethoxazole Control
Conc. (ng/mL)
120.00
100.00
80.00
60.00
40.00
20.00
0.00
6/21/12 9:36
6/21/12 21:36
6/22/12 9:36
6/22/12 21:36
6/23/12 9:36
6/23/12 21:36
6/24/12 9:36
Sampling Time
Control
MDL

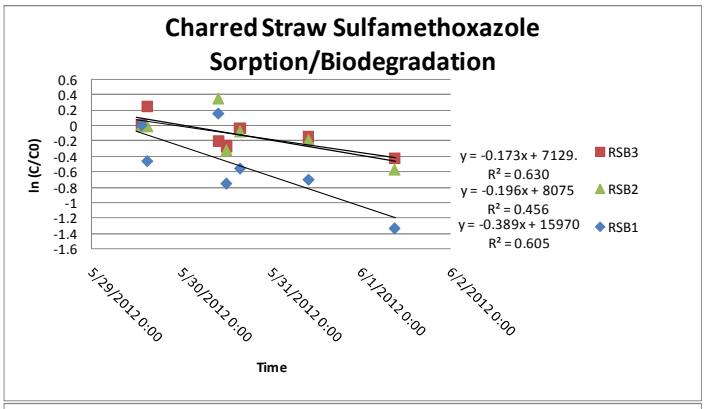


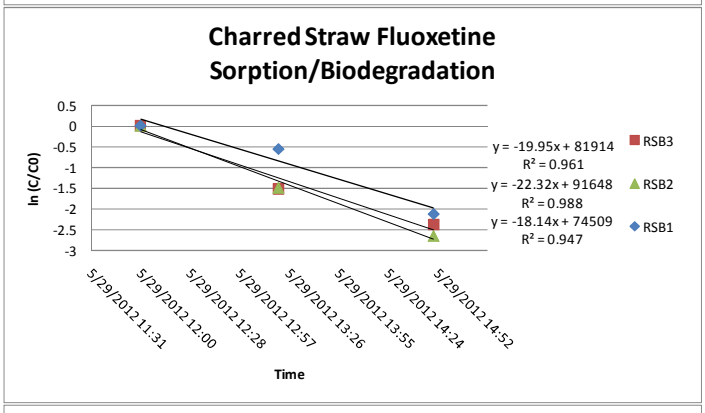


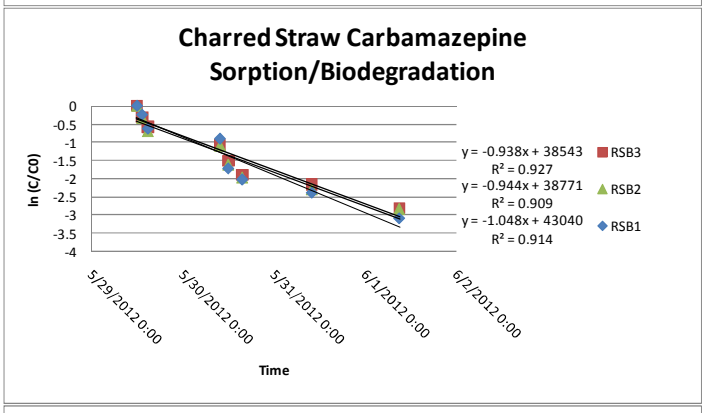
M 1st Order Graphs

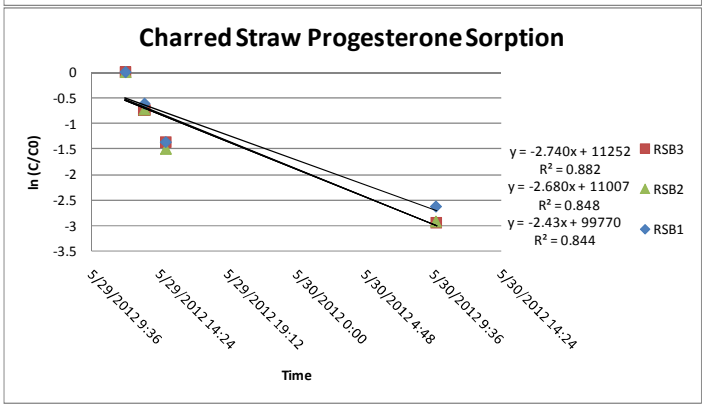


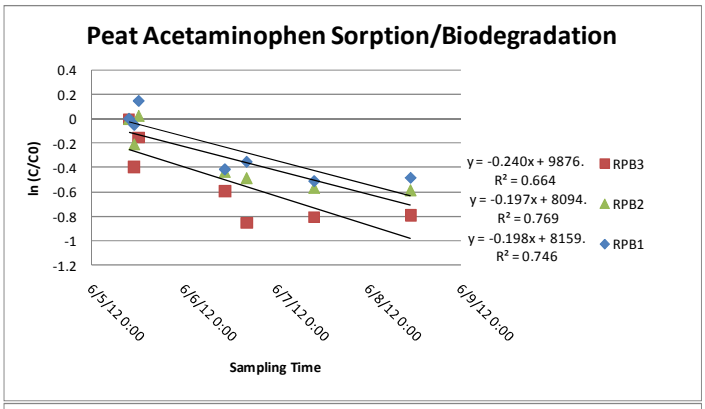


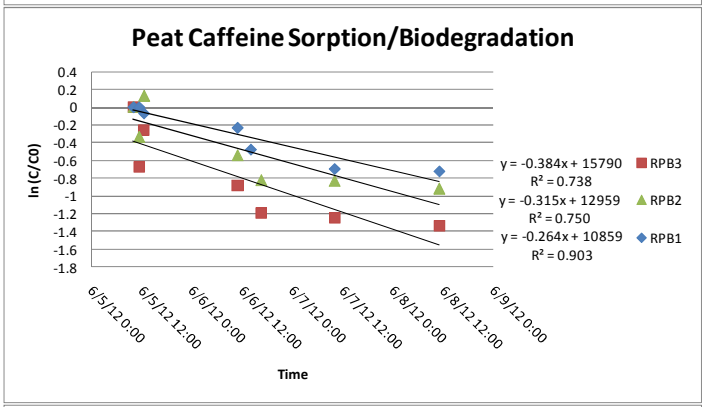

Charred Straw Sulfamethoxazole Sorption/Biodegradation
ln (C/C0)
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
5/29/2012 0:00
5/30/2012 0:00
5/31/2012 0:00
6/1/2012 0:00
6/2/2012 0:00
Time
y = -0.173x + 7129.
R² = 0.630
y = -0.196x + 8075
R² = 0.456
y = -0.389x + 15970
R² = 0.605
RSB3
RSB2
RSB1

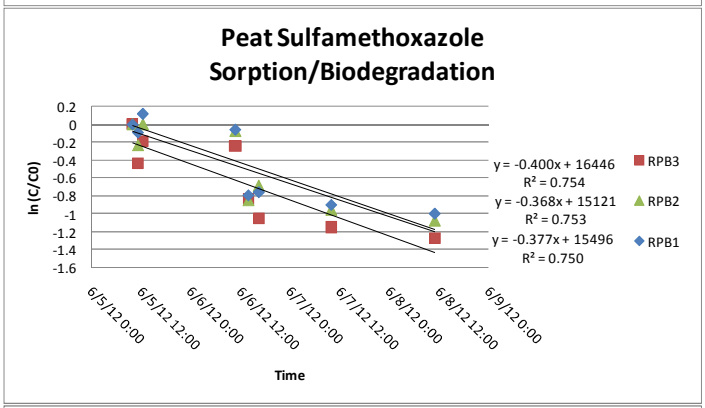

Charred Straw Fluoxetine Sorption/Biodegradation
ln (C/C0)
0.5
0
-0.5
-1
-1.5
-2
-2.5
-3
5/29/2012 11:31
5/29/2012 12:00
5/29/2012 12:28
5/29/2012 12:57
5/29/2012 13:26
5/29/2012 13:55
5/29/2012 14:24
5/29/2012 14:52
Time
y = -19.95x + 81914
R² = 0.961
y = -22.32x + 91648
R² = 0.988
y = -18.14x + 74509
R² = 0.947
RSB3
RSB2
RSB1

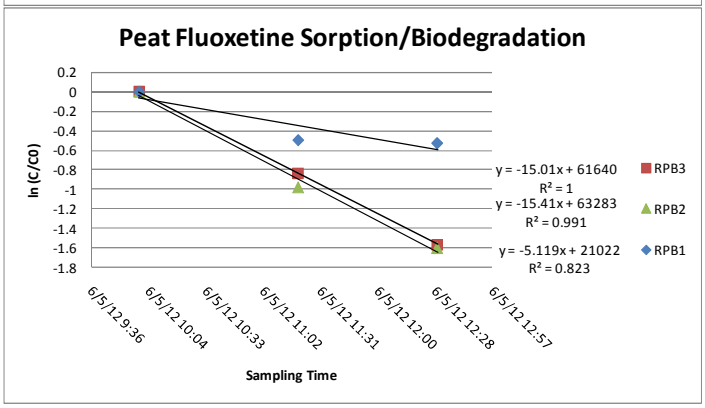

Charred Straw Carbamazepine Sorption/Biodegradation
ln (C/C0)
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
5/29/2012 0:00
5/30/2012 0:00
5/31/2012 0:00
6/1/2012 0:00
6/2/2012 0:00
Time
y = -0.938x + 38543
R² = 0.927
y = -0.944x + 38771
R² = 0.909
y = -1.048x + 43040
R² = 0.914
RSB3
RSB2
RSB1

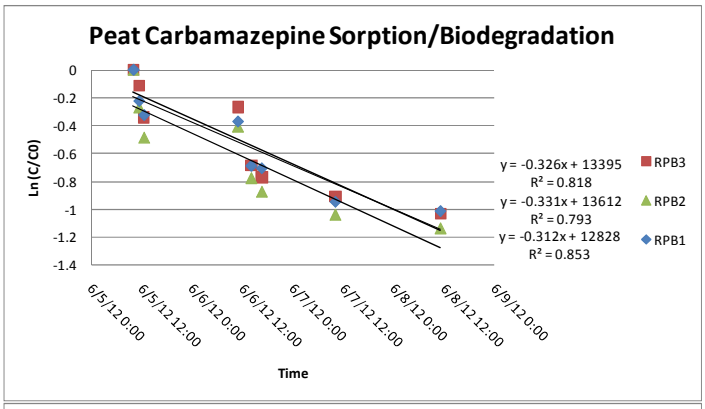

Charred Straw Progesterone Sorption
ln (C/C0)
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
5/29/2012 9:36
5/29/2012 14:24
5/29/2012 19:12
5/30/2012 0:00
5/30/2012 4:48
5/30/2012 9:36
5/30/2012 14:24
Time
y = -2.740x + 11252
R² = 0.882
y = -2.680x + 11007
R² = 0.848
y = -2.43x + 99770
R² = 0.844
RSB3
RSB2
RSB1

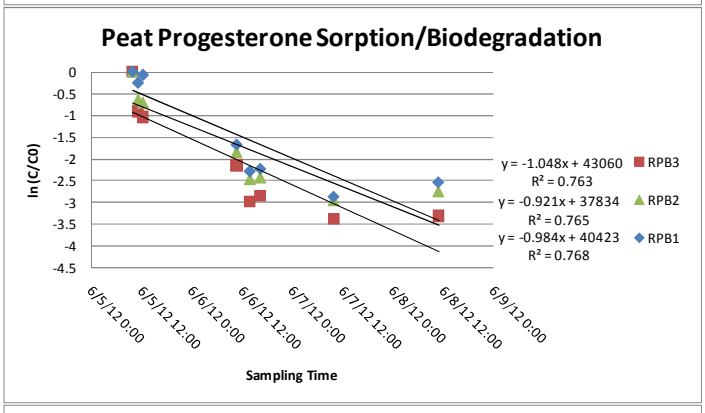

Peat Acetaminophen Sorption/Biodegradation
ln (C/C0)
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
6/5/12 0:00
6/6/12 0:00
6/7/12 0:00
6/8/12 0:00
6/9/12 0:00
Sampling Time
y = -0.240x + 9876.
R² = 0.664
y = -0.197x + 8094.
R² = 0.769
y = -0.198x + 8159.
R² = 0.746
RPB3
RPB2
RPB1

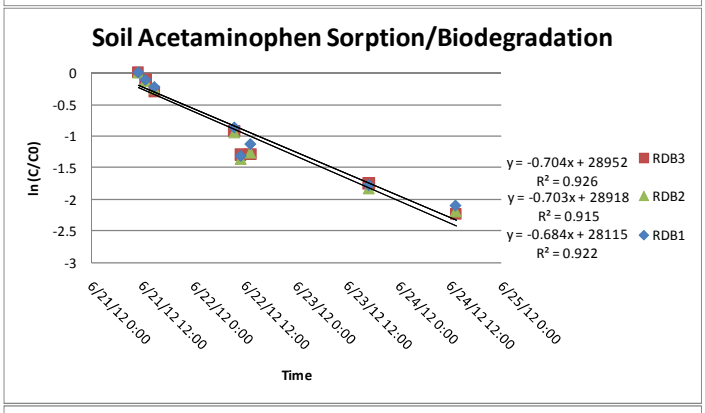

Peat Caffeine Sorption/Biodegradation
ln (C/C0)
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
6/5/12 0:00
6/5/12 12:00
6/6/12 0:00
6/6/12 12:00
6/7/12 0:00
6/7/12 12:00
6/8/12 0:00
6/8/12 12:00
6/9/12 0:00
Time
y = -0.384x + 15790
R² = 0.738
y = -0.315x + 12959
R² = 0.750
y = -0.264x + 10859
R² = 0.903
RPB3
RPB2
RPB1

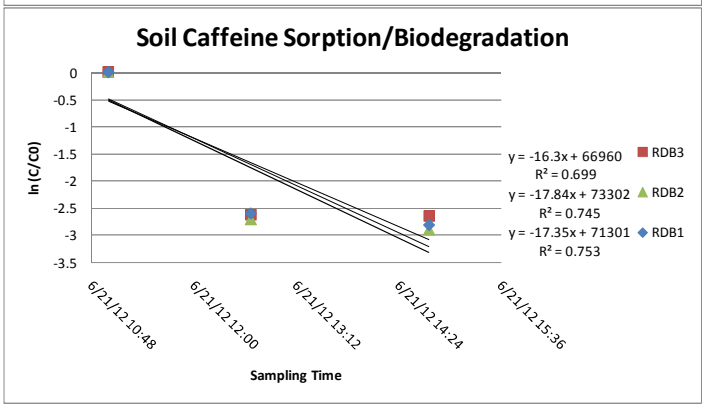

Peat Sulfamethoxazole
Sorption/Biodegradation
ln (C/C0)
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
6/5/12 0:00
6/5/12 12:00
6/6/12 0:00
6/6/12 12:00
6/7/12 0:00
6/7/12 12:00
6/8/12 0:00
6/8/12 12:00
6/9/12 0:00
Time
y = -0.400x + 16446
R² = 0.754
y = -0.368x + 15121
R² = 0.753
y = -0.377x + 15496
R² = 0.750
RPB3
RPB2
RPB1

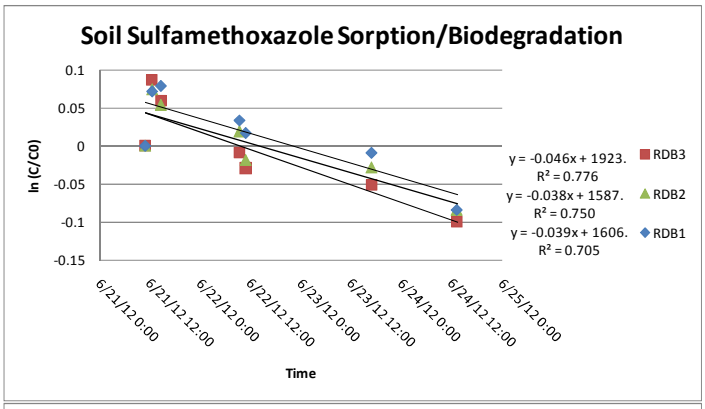

Peat Fluoxetine Sorption/Biodegradation
ln (C/C0)
0.2
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
-1.6
-1.8
6/5/12 9:36
6/5/12 10:04
6/5/12 10:33
6/5/12 11:02
6/5/12 11:31
6/5/12 12:00
6/5/12 12:28
6/5/12 12:57
Sampling Time
y = -15.01x + 61640
R² = 1
y = -15.41x + 63283
R² = 0.991
y = -5.119x + 21022
R² = 0.823
RPB3
RPB2
RPB1

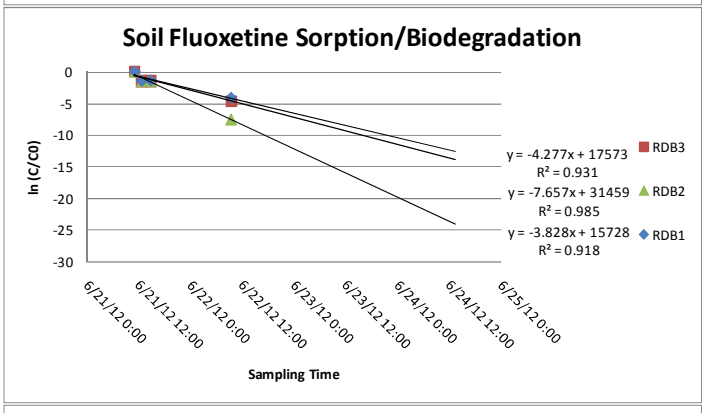

Peat Carbamazepine Sorption/Biodegradation
Ln (C/C0)
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
-1.4
6/5/12 0:00
6/5/12 12:00
6/6/12 0:00
6/6/12 12:00
6/7/12 0:00
6/7/12 12:00
6/8/12 0:00
6/8/12 12:00
6/9/12 0:00
Time
y = -0.326x + 13395
R² = 0.818
y = -0.331x + 13612
R² = 0.793
y = -0.312x + 12828
R² = 0.853
RPB3
RPB2
RPB1

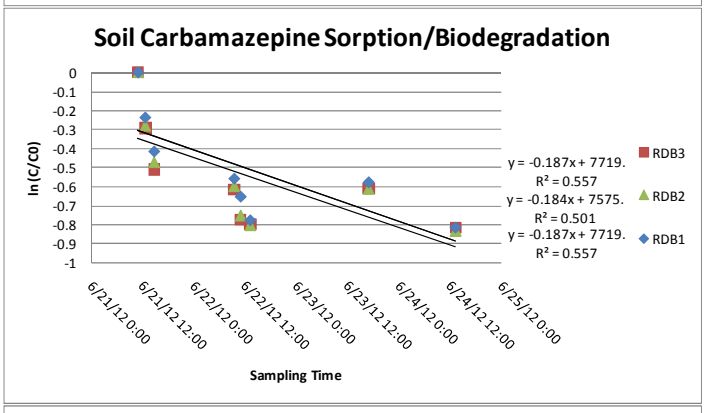

Peat Progesterone Sorption/Biodegradation
ln (C/C0)
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
6/5/12 0:00
6/5/12 12:00
6/6/12 0:00
6/6/12 12:00
6/7/12 0:00
6/7/12 12:00
6/8/12 0:00
6/8/12 12:00
6/9/12 0:00
Sampling Time
y = -1.048x + 43060
R² = 0.763
y = -0.921x + 37834
R² = 0.765
y = -0.984x + 40423
R² = 0.768
RPB3
RPB2
RPB1

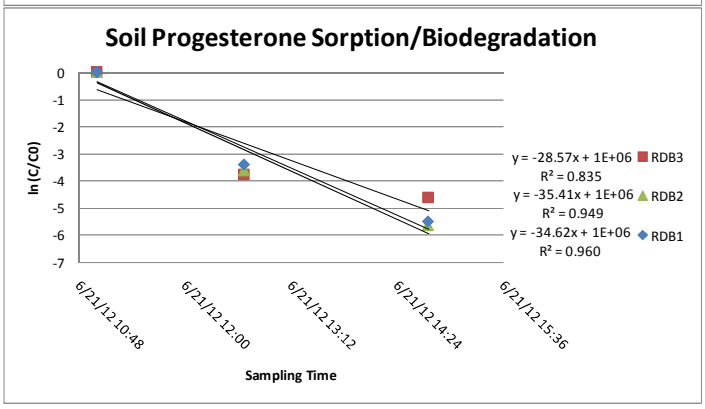

Soil Acetaminophen Sorption/Biodegradation
ln (C/C0)
0
-0.5
-1
-1.5
-2
-2.5
-3
6/21/12 0:00
6/21/12 12:00
6/22/12 0:00
6/22/12 12:00
6/23/12 0:00
6/23/12 12:00
6/24/12 0:00
6/24/12 12:00
6/25/12 0:00
Time
y = -0.704x + 28952
R² = 0.926
y = -0.703x + 28918
R² = 0.915
y = -0.684x + 28115
R² = 0.922
RDB3
RDB2
RDB1


Soil Caffeine Sorption/Biodegradation
ln (C/C0)
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
6/21/12 10:48
6/21/12 12:00
6/21/12 13:12
6/21/12 14:24
6/21/12 15:36
Sampling Time
y = -16.3x + 66960
R² = 0.699
y = -17.84x + 73302
R² = 0.745
y = -17.35x + 71301
R² = 0.753
RDB3
RDB2
RDB1


Soil Sulfamethoxazole Sorption/Biodegradation
ln (C/C0)
0.1
0.05
0
-0.05
-0.1
-0.15
6/21/12 0:00
6/21/12 12:00
6/22/12 0:00
6/22/12 12:00
6/23/12 0:00
6/23/12 12:00
6/24/12 0:00
6/24/12 12:00
6/25/12 0:00
Time
y = -0.046x + 1923.
R² = 0.776
y = -0.038x + 1587.
R² = 0.750
y = -0.039x + 1606.
R² = 0.705
RDB3
RDB2
RDB1


Soil Fluoxetine Sorption/Biodegradation
ln (C/C0)
0
-5
-10
-15
-20
-25
-30
6/21/12 0:00
6/21/12 12:00
6/22/12 0:00
6/22/12 12:00
6/23/12 0:00
6/23/12 12:00
6/24/12 0:00
6/24/12 12:00
6/25/12 0:00
Sampling Time
y = -4.277x + 17573
R² = 0.931
y = -7.657x + 31459
R² = 0.985
y = -3.828x + 15728
R² = 0.918
RDB3
RDB2
RDB1


Soil Carbamazepine Sorption/Biodegradation
ln (C/C0)
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
6/21/12 0:00
6/21/12 12:00
6/22/12 0:00
6/22/12 12:00
6/23/12 0:00
6/23/12 12:00
6/24/12 0:00
6/24/12 12:00
6/25/12 0:00
Sampling Time
y = -0.187x + 7719.
R² = 0.557
y = -0.184x + 7575.
R² = 0.501
y = -0.187x + 7719.
R² = 0.557
RDB3
RDB2
RDB1


Soil Progesterone Sorption/Biodegradation
ln (C/C0)
0
-1
-2
-3
-4
-5
-6
-7
6/21/12 10:48
6/21/12 12:00
6/21/12 13:12
6/21/12 14:24
6/21/12 15:36
Sampling Time
y = -28.57x + 1E+06
R² = 0.835
y = -35.41x + 1E+06
R² = 0.949
y = -34.62x + 1E+06
R² = 0.960
RDB3
RDB2
RDB1

N Bromide Tracer Results